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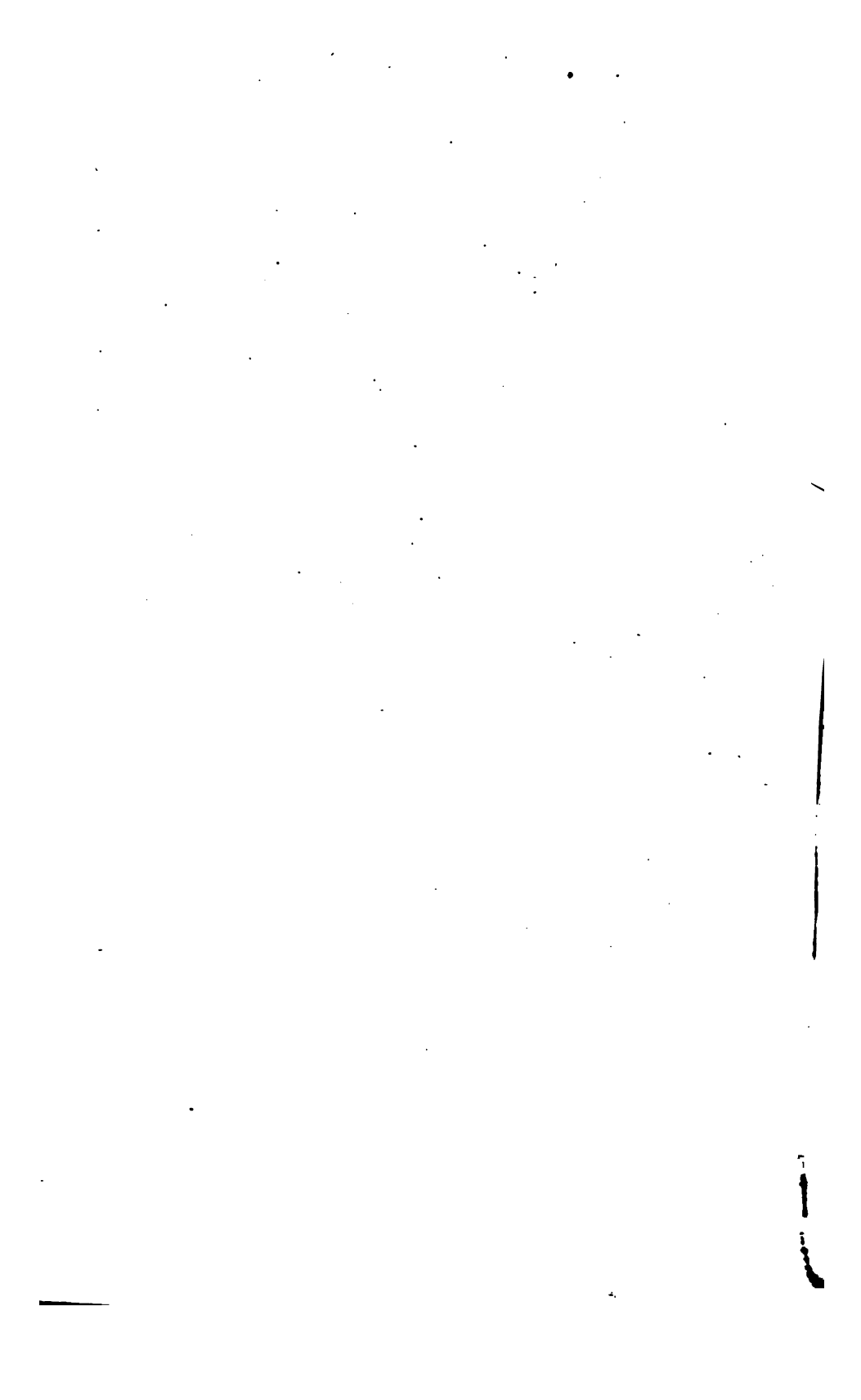
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**A**  
**PRACTICAL TREATISE**  
**OF**  
**CHEMICAL ANALYSIS.**



A  
PRACTICAL TREATISE  
OF  
CHEMICAL ANALYSIS,

INCLUDING

TABLES FOR CALCULATIONS IN ANALYSIS.

BY H. ROSE.

TRANSLATED FROM THE FRENCH AND FROM THE FOURTH GERMAN EDITION.

With Notes and Additions,

BY A. NORMANDY.

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## QUANTITATIVE ANALYSIS.

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I INTEND to describe in this Volume the methods employed, after having ascertained the nature of the constituents of compound substances, to separate them from each other, and to determine their quantity, that is, their respective proportions.

In the plan which I have adopted, those substances called bases will be first treated of, and those whose compounds have acid properties will come afterwards. Under the head Potassium, I give the means of determining potash quantitatively, and under the head Sodium, I indicate not only the method of determining soda quantitatively, but also how the operator must proceed to separate that alkali from potash, and to determine the respective quantity of these two substances. In the same manner, in the whole series of simple bodies, I first show the processes by which the quantity of each body can be determined, after which I describe the methods which must be adopted to separate it from all the preceding bodies in the combinations of which it may enter. By this plan, all the methods which the operator may wish to employ in any given quantitative analysis, can be found at once, and without difficulty.

## CHAPTER I.

## POTASSIUM.

## DETERMINATION OF POTASSIUM AND OF POTASH.

WHEN the quantity of potassium or of potash has to be estimated in a substance, and if it has not to be separated from any other base, the combination best adapted for the purpose is SULPHATE OF CARBONATE OF POTASH, OR A CHLORIDE OF POTASSIUM; and from the weight of these salts the quantity of potassium or of potash is calculated from the tables for calculations in analysis at the end of this work.

If potash be contained in a solution in the state of SULPHATE OF POTASH, it should be evaporated to dryness at a gentle heat; the residuum is ignited and weighed. This operation is best performed in a platinum capsula, or else in one of porcelain, especially if the liquor contains nitric and muriatic acid at the same time. The dry mass is detached as completely as possible from the capsula, with the help of a platinum spatula, and transferred to a weighed platinum capsula or crucible. In order to be sure that nothing is left in the vessel, it should be washed with water, and the washing transferred to the platinum capsula or crucible; the whole is then carefully evaporated and the residuum ignited.

The sulphate of potash must, however, be kept for a pretty long time exposed to a good heat previous to its ignition, in order to avoid the decrepitation which might then take place, and which might occasion a considerable

loss.<sup>1</sup> If the solution contained an excess of sulphuric acid, the residuum after evaporation is bisulphate of potash, which it is extremely difficult to deprive of its excess of sulphuric acid by ignition in a platinum crucible. It can, however, be easily and completely converted into the neutral sulphate of potash by the method prescribed by Berzelius, and which consists in cautiously exposing it to a red heat, and then introducing a small piece of dry carbonate of ammonia upon a small strip of platinum foil, into the crucible, putting the cover loosely over the whole, and then giving a strong heat. The excess of sulphuric acid volatilises easily in an atmosphere of carbonate of ammonia,<sup>2</sup> and neutral sulphate of potash remains behind. The mass, which before was easily fusible, has now become extremely difficult to fuse.

If potassium be contained in the solution in the state of CHLORIDE OF POTASSIUM, the solution must likewise be evaporated to dryness, and the dried mass is then heated in a small counterpoised platinum crucible to incipient redness.<sup>3</sup> It is necessary, during this operation, to keep the cover on the crucible, because, in contact with the air, a strong ignition might volatilise a small quantity of chloride of potassium.

When the liquor contains CARBONATE OF POTASH only, it may also be evaporated to dryness, and the carbonate of potash ignited in the platinum crucible. But as this salt is very deliquescent, it is difficult, after its ignition, to determine its proportion accurately enough for weighing it. It is better, therefore, to add muriatic acid to the liquor before evaporating it, and by means of the tables for calculations in analysis, the quantity of carbonate of potash may be calculated from the

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<sup>1</sup> During ignition the cover should be kept on for fear of loss from decrepitation, since even the crystals of sulphate of potash which have been kept for a long time at a drying heat, are liable to decrepitate when a stronger heat is applied; wherefore the heat should be very gradually increased, and the cover carefully kept on, as we have said.—ED.

<sup>2</sup> The excess of sulphuric acid combines with the ammonia, and is volatilised in the state of sulphate of ammonia.—ED.

<sup>3</sup> Chloride of potassium should, like sulphate of potash, be carefully and thoroughly dried before ignition, because it is a decrepitating salt.—ED.



chloride of potassium obtained. The operator may also begin, first, by weighing the carbonate of potash which has been evaporated to dryness and ignited; then, treating it in the platinum crucible by muriatic acid, carefully evaporating the whole to dryness, igniting it, and calculating from the quantity of the chloride of potassium obtained what was that of the carbonate. This last method, however, requires numerous precautions: for example, the muriatic acid must be added to the carbonate of potash by portions as small as possible at a time, otherwise the disengagement of carbonic acid would occasion projections, and a considerable loss of substance might be the result. It is necessary, also, whilst adding the acid, to cover the crucible with a watch glass, or some such concave piece of glass, in order to avoid all loss by the effervescence. After saturation, the glass plate is washed and the liquor is cautiously evaporated.

If potash be combined with nitric acid in the liquor, it is evaporated to dryness at a moderate heat, which must not be much above the temperature of boiling water, and to the action of which it is abandoned until it is found that the weight of the nitrate remains constant. The solid nitrate of potash thus obtained must not be heated to fusion, because part of it might be decomposed by a prolonged fusion, and if the salts contain traces of organic substances, their presence determines the decomposition of a portion of the nitric acid, and detonation takes place which may cause the loss of part of the mass.

When potash is combined with another acid, the quantity of this alkali is determined by certain methods which will be subsequently described at length. I shall indicate here only those by means of which their quantity may be determined when it is combined with those acids which, in a free state, are soluble in alcohol, which is the case with most of them. When this occurs, the combination containing potash is then dissolved in water, and an excess of solution of *chloride of platinum* is added to the liquor, the whole is most cautiously evaporated almost to dryness. The double chloride of platinum and potassium

formed, and which is sparingly soluble, separates the very instant that the solution of chloride of platinum is poured in, but if the liquor be too dilute this separation takes place only during the evaporation. When the mass is nearly dry, some weak alcohol is poured upon it, or if the liquor has been reduced in bulk by evaporation strong alcohol is used. The double chloride of platinum and of potassium, which is not soluble in weak alcohol, is collected upon a weighed filter<sup>1</sup> washed with weak alcohol, and cautiously dried, and from its weight the quantity of potash is calculated. If the substance containing the potash to be analysed is soluble in either weak or strong alcohol, an alcoholic solution of chloride of platinum may be added to the alcoholic solution of the substance, the precipitate of potassio-chloride of platinum produced is then collected on a filter and washed with weak alcohol. The acid with which the potash was combined may be found dissolved in the liquor filtered from the precipitate.

\* When the substance under examination contains only a small quantity of potash, and consequently the quantity of potassio-chloride obtained is so small that it does not exceed a few centigrammes, it is not necessary to collect it on a weighed filter. An ordinary filter may then be used, provided it be not too large. After having washed the salt with weak alcohol, it is ignited, but cautiously, else the vapours of chlorine might carry away a little undecomposed chloride, and even a little metallic platinum. The salt enveloped in the filter should be put in a platinum crucible carefully covered, and exposed for a long time to a moderate heat. The filter is thus carbonised, and the salt undergoes decomposition without a single particle being mechanically carried off. The cover is then partially removed, and the fire augmented, so as to incinerate the charcoal of the filter; water is next poured in the crucible,

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<sup>1</sup> This essential precaution of a weighed filter is performed by folding the filter, introducing it in a platinum crucible previously counterpoised with its cover, and exposed to a heat of about 212°. The closed crucible is then taken out and placed under a bell, by the side of a capsula containing concentrated sulphuric acid, until quite cold, and then it is immediately weighed.—Ed.

which dissolves the chloride of potassium, leaving platinum in very fine powder, and which, by reason of its great specific gravity, remains at the bottom. The washing is continued until, by testing it with solution of nitrate of silver, it no longer becomes turbid. The platinum is then dried, ignited, weighed; and from its quantity, that of the potassium or of the potash can be calculated by means of the tables at the end.

\* This method, however, should be altogether rejected when the quantity of potassio-chloride of platinum amounts to one, and, *a fortiori*, to several decigrammes, for a correct result could not thus be obtained except by the most extreme care and the greatest circumspection. By ignition the chloride of potassium melts, and so completely shelters the charcoal of the filter, that it cannot subsequently be incinerated when the cover is removed from the crucible. The incineration is even difficult if, after having dissolved the greatest part of the chloride of potassium by washing it with water, the residuum is dried and ignited.

## CHAPTER II.

## SODIUM.

## DETERMINATION OF SODIUM AND OF SODA.

WHEN sodium is contained in the state of oxysalt, or of chloride of sodium in a liquor which contains no other substance from which it has to be separated, its quantity is determined in the same manner as that of potassium. During the ignition of sulphate of soda, no decrepitation need be apprehended. If there be an excess of sulphuric acid, the acid sulphate of soda is to be treated, like that of potash, by carbonate of ammonia, in order to convert it into the neutral sulphate.

CHLORIDE OF SODIUM, like *chloride of potassium*, must not be exposed to a strong red heat, because otherwise a small portion might be volatilised,<sup>1</sup> though this salt is less volatile than chloride of potassium.

If soda is in the state of CARBONATE OF SODA, the operation by which its quantity is determined is less difficult than for the corresponding carbonate of potash, because carbonate of soda does not attract moisture so rapidly nor so easily as carbonate of potash. It is advisable, however, to heat the carbonate of soda until it fuses in the counterpoised platinum crucible.

\* When soda is combined with acids which, in the free state,

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<sup>1</sup> The operator must bear in mind, that if chloride of sodium is not thoroughly dried before ignition it will decrepitate, and there will be danger of losing portions of it.—Ed.

are soluble in weak alcohol, it cannot be separated, like potash, by means of chloride of platinum, because the double chloride of sodium and platinum is soluble in aqueous alcohol.<sup>1</sup>

#### SEPARATION OF SODA FROM POTASH.

When a liquor contains soda and potash at the same time, the two alkalies may be separated, and their proportions determined exactly, in the following manner:—Both salts are converted into chlorides, the solution is evaporated to dryness, the residuum is heated in a counterpoised platinum crucible to incipient redness, and weighed; the salt obtained is then to be mixed with three times and three-fourths its weight of crystallised soda-chloride of platinum, which quantity is exactly sufficient to convert the saline mass under examination into potash-chloride of platinum, supposing that it consists altogether of chloride of potassium.

\* [If soda-chloride of platinum is not at hand, the operator may take a solution of chloride of platinum, to which a little, but not too much, chloride of sodium is added, which answers the same purpose.] The mixture is dissolved in a very small quantity of water, and evaporated almost to dryness, at a very gentle heat in a platinum or in a porcelain capsula; it is next to be treated by alcohol, containing about sixty per cent. of alcohol, which dissolves the chloride of sodium, and the excess of soda chloride of platinum. The potash-chloride of platinum which has formed remains insoluble. It is collected on a weighed filter, and washed with aqueous alcohol; and lastly, it is dried at a very gentle heat, until after being weighed several times the weight remains constant. From the potash-chloride of platinum thus obtained, the quantity of chloride of potassium contained in the saline mixture under examination is calculated. As to the quantity of chloride of sodium, it may be found by deducting the weight of the chloride of potassium from that of the two metallic chlorides.

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<sup>1</sup> We should remark, that even potassio-chloride of platinum is not altogether insoluble in alcohol.—Ed.

Chloride of platinum cannot be used so advantageously as the double chloride of sodium and platinum, because the first of these salts is more liable to be decomposed by alcohol. \* [If, however, the quantity of chloride of sodium is considerable, compared with that of the chloride of potassium, a solution of the simple chloride of platinum may very well be employed.]

\* This method, however, cannot be resorted to for the purpose of determining immediately the quantity of the two alkalies instead of estimating that of the soda by the loss, or deduction from the weight. In such cases, chloride of platinum only can be employed for precipitating the potash. After having added it, the solution is cautiously evaporated almost to dryness, alcohol is then poured upon the residuum, and the potash-chloride of platinum produced is separated by filtering. A little muriatic acid is then added to the filtered liquor, it is diluted with water, and the greater portion of the alcohol is driven off by heating it gently. An excess of solution of chloride of platinum is next added, and a current of sulphuretted hydrogen is carefully passed through the liquor.<sup>1</sup> The sulphuret of platinum thus precipitated, is separated by filtering, and rapidly washed with cold water. The filtered liquid must be evaporated slowly to dryness, and after heating the chloride of sodium obtained to incipient redness, it is weighed.

\* The platinum of the excess of chloride of platinum may be precipitated by other means than by sulphuretted hydrogen. After having separated the potash-chloride of platinum by filtering, the liquor is evaporated to dryness, and the residuum sufficiently, but not too strongly ignited, by which means the platinum of the chloride of platinum is reduced. The ignited mass is treated by water, which dissolves the chloride of sodium, and leaves the reduced platinum, which may be collected on a filter, after which the solution of chloride of sodium is evaporated to dryness.

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<sup>1</sup> It is absolutely necessary that the solution should be sufficiently diluted, otherwise the sulphuret may escape complete precipitation, and the muriatic acid added as above must be in sufficient quantity to give an acid reaction to the liquor, in order to prevent the precipitation of certain oxydes which otherwise might, if present, be precipitated by the sulphuretted hydrogen.—Ed.

If the potash and soda are in the state of sulphates, they must be converted into chlorides before they can be separated by the process just described. The best way of effecting this conversion will be described farther on. (See the article on SULPHUR.)

\* According to Serullas, PERCHLORIC ACID, and some PERCHLORATES may be resorted to as an easy method of separating potash from soda. Perchlorate of potash is very sparingly soluble in water, and altogether insoluble in alcohol, whilst perchlorate of soda is very soluble in both these menstrua, which appears also to be the case with most of the combinations of perchloric acid with the bases.<sup>1</sup>

\* If perchloric acid is added to a solution of salts of potash and soda, for the purpose of separating them from each other, the solution must first be carefully evaporated nearly to dryness, and the residuary mass is treated by alcohol, in which the perchlorate of potash formed is insoluble, but which dissolves the perchlorate of soda formed at the same time, and also the acid which was combined with the two alkalies before treatment.<sup>2</sup>

\* When these two alkalies are contained in an aqueous solution in the state of *metallic chlorides*, perchlorate of silver may be used to separate them from each other in the following manner:—An excess of an aqueous solution of perchlorate of silver is added to that of the metallic chlorides. The chloride of silver thus produced is separated by filtering and washed with hot water, in order to dissolve completely the perchlorate of potash formed. The quantity of chloride of silver obtained is

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<sup>1</sup> The method recommended by M. Nativelle for the preparation of perchloric acid as a reagent, consists in introducing in a retort 500 grammes of perchlorate of potash, and 1000 grammes of pure sulphuric acid, previously diluted with 100 grammes of water. The whole is mixed by agitating, and heated to about 300° Fahr. The perchloric acid distils in an almost pure state, being contaminated only by a little chlorine and a little sulphuric acid. It is to be agitated successively with small quantities of oxyde of silver and of baryta, and it is distilled. If the operation has been well conducted, 150 grammes of a pure and colourless acid are obtained.—Ed.

<sup>2</sup> The precipitated perchlorate of potash may be collected on a filter, washed with alcohol, dried and exposed carefully at a dark red heat; chloride of potassium will then be left, which may be weighed, and from which the quantity of potassium or of potash may be easily calculated.—Ed.

then determined, and from it that of the chlorine which was combined with the alkalisable metals. The liquor filtered from the chloride of silver is evaporated to dryness, and the dry mass is treated by strong alcohol, which dissolves the perchlorate of soda and the excess of perchlorate of silver, but leaves the perchlorate of potash untouched, and which is to be washed with alcohol. This insoluble perchlorate of potash is carefully exposed to a red heat, by which means it is converted, under disengagement of oxygen, into chloride of potassium, the weight of which may be determined, and from which the quantity of the potash may be calculated. The alcoholic solution of the perchlorates of soda and of silver is also evaporated to dryness, the dry residuum is ignited, and by washing, the chloride of sodium produced may be separated from the chloride of silver, the filtered liquid containing the chloride of sodium in solution is cautiously evaporated to dryness in order to obtain the weight of this salt.

\* If the potash and soda which it is intended to separate from each other are in the state of sulphates, perchlorate of baryta is added to the solution of the sulphates of alkalies. After separating the sulphate of baryta which will have formed, and washing it with hot water, the filtered liquid is evaporated to dryness, and the perchlorate of potash is separated by alcohol. The alcoholic solution of the perchlorates of soda and of baryta is evaporated to dryness in order to expel the alcohol. Water is next added, and the baryta is precipitated by sulphuric acid. The liquor filtered from the sulphate of baryta is evaporated to dryness, and the sulphate of soda is then treated by carbonate of ammonia before determining its quantity.<sup>1</sup>

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<sup>1</sup> The salt of soda is thus converted into neutral sulphate of soda, in which state it is weighed, for the purpose of estimating the quantity of soda. The process being the same as that described for potash, page 2.

M. Barreswill proposed to determine the quantity of caustic soda in soda-ash by means of chloride of barium, an excess of which is to be poured in the solution of the sample, and filtering. If the filtrate has an alkaline reaction, the presence of caustic soda is inferred, and its quantity may be determined in the filtrate as directed above, or by the alkali-meter, as will be shown farther on.—Ed.



## CHAPTER III.

## LITHIUM.

## DETERMINATION OF LITHIUM AND OF LITHIA.

\* WHEN lithia has not to be separated from any other base, its quantity is determined by the same method which is employed for potash and for soda.

If lithia is in combination with sulphuric acid, it is not necessary to treat the sulphate of lithia by exposure to a red heat with carbonate of ammonia, because there is no bisulphate of lithia,<sup>1</sup> and the red heat alone is sufficient to dissipate an excess of sulphuric acid. As chloride of lithium rapidly deliquesces in the air it cannot be weighed exactly, on that account, and it is well, therefore, to convert it into sulphate of lithia.

\* If it be desired to weigh it as chloride of lithium, the operator must not ignite it too strongly, because a small portion of it might thus be volatilised. This salt is less volatile than chloride of potassium, but more so than chloride of sodium.

Yet if the quantity of lithia in a liquor is very small, and if this liquor contains potash and soda besides, Berzelius indicates a peculiar process for the estimation of the lithia. A little pure phosphoric acid and an excess of pure carbonate of soda is to be added to the liquor, and the whole is evaporated to dryness.

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<sup>1</sup> Therefore, when the solution under examination contains no other base from which it has to be first separated, it may at once be converted into sulphate by simply adding sulphuric acid to the solution, evaporating to dryness, and igniting the dry mass to expel the excess of sulphuric acid, and weighing.—ED.

During the evaporation, and when it has reached a certain degree of concentration, the liquor gradually becomes turbid, and after the complete exsiccation of the salt, and dissolving thereof in cold water, there remains a white powder which is insoluble in the mother-water, which is rich in phosphate of soda, and which white powder slowly subsides at the bottom.<sup>1</sup> This powder is washed with cold water, but the washing must not be continued too long, because a small portion of the powder is dissolved by it; hot water must not be used, because it is more soluble in it than in cold water. This powder is a neutral double phosphate of lithia and of soda. When it is dry it is ignited, and from its weight the quantity of lithia is calculated.

\* It is absolutely necessary that the liquor from which lithia is to be precipitated according to this process should contain no other bases than alkalies. But in order to be sure that the ignited and weighed salt is really a double phosphate of soda and lithia, it should be examined according to the methods which have been indicated in Vol. I. p. 18, because it might easily be confounded with the insoluble combinations of phosphoric acid and lime or magnesia.

#### SEPARATION OF LITHIA FROM POTASH.

In order to separate lithia from potash so as to be able to estimate it quantitatively, the potash should be precipitated by the process which is employed to separate it from soda, and which has been described page 8. To the liquor filtered from the potassio-chloride of platinum obtained, a little muriatic acid is added, the liquor is next diluted with water, and gently heated until the greater part of the alcohol is expelled, after which a current of sulphuretted hydrogen is passed through it in order to precipitate the platinum in solution. The sulphuret of platinum thus produced is collected upon a filter and washed rapidly with cold water; the filtered liquor is then heated until

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<sup>1</sup> The double phosphate of soda and lithia is insoluble in water which contains any phosphate in solution, and almost so in cold water.—ED.

all smell of sulphuretted hydrogen has disappeared, and lithia is precipitated therefrom in the state of double phosphate of soda and lithia, in the manner which has been just mentioned.

The liquor filtered from the potash-chloride of platinum may also be evaporated to dryness, and the dry mass strongly ignited, by which the chloride of platinum is reduced. The ignited mass is then treated by water, and the reduced platinum being separated by filtering, the lithia may be precipitated from the filtered liquor.

\* If the simple chloride of platinum has been used instead of the soda-chloride of platinum, to effect the separation, the operator, after first eliminating the excess of potash-chloride of platinum and of the platinum, may obtain the chloride of lithium by simple evaporation and determine its quantity, or else convert it into sulphate of lithia. This method is preferable to that which I have related, because the estimation of lithia as phosphate of soda and lithia is always attended with some uncertainty.

\* Lithia might also be separated from potash in the same manner as this latter substance is separated from soda, namely, by perchloric acid; for perchlorate of lithia, like perchlorate of soda, is soluble in water and in alcohol.

#### SEPARATION OF LITHIA FROM SODA.

The separation of lithia from soda is effected in the following manner:—the weight of the two alkalies in the state of sulphates or carbonates, or of chlorides, must first be ascertained. The mixture is next dissolved, and the lithia is precipitated as phosphate of soda and lithia. From the quantity of this double salt, after ignition, that of the lithia-salt is calculated, and the loss on the original weight represents the quantity of the soda-salt.<sup>1</sup>

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<sup>1</sup> The double phosphate of lithia and soda after ignition, contains 12.32 per cent of lithia.—Ed.

## SEPARATION OF LITHIA FROM POTASH AND SODA.

If these three alkalies, namely : potash, soda, and lithia, exist simultaneously in a solution, the method for estimating their respective quantities is the following : the weight of these mixed salts must first be determined in the state of metallic chlorides. The potash is next precipitated by a solution of chloride of platinum in the state of potash-chloride of platinum, from which the quantity of that alkali is calculated ; it is then easy to ascertain what was the weight of the potash-salt which was contained in the saline mixture first weighed. The liquor is next filtered, and the platinum which it holds in solution is eliminated either by passing a current of sulphuretted hydrogen through it, or else by evaporating it to dryness and igniting the dry residuum, and lastly, the lithia is precipitated in the state of phosphate of soda and lithia, from which the quantity of lithia and of the lithic salt may be calculated, which quantities deducted from that of the mixed salts first weighed, gives the weight of the soda-salt.

\* From a mixture of these three alkalies, the potash may also be separated by perchloric acid, and the lithia may afterwards be separated from the soda in the way which we have just described.<sup>1</sup>

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<sup>1</sup> M. Rammelsberg proposed to separate lithia from soda in the analysis of minerals, in which lithia is accompanied by the latter substance, by treating the chloride of these substances with a mixture of alcohol and of ether in the anhydrous state ; the chloride of lithium dissolves completely in it, whilst only a trace of chloride of sodium is taken up in the solution.—ED.

## CHAPTER IV.

## BARIUM.

## DETERMINATION OF BARIUM AND OF BARYTA.

Few substances can be so accurately determined and easily separated from a great number of other bodies as baryta.

The quantity of baryta is determined by pouring dilute sulphuric acid in the solution which contains it until it ceases to produce a precipitate. This precipitate is sulphate of baryta, which salt is completely insoluble in water and in all dilute acids. It is washed, exposed to a low red heat and weighed. From its weight the quantity of the baryta is calculated. The filter may be burnt along with the precipitate, and it may be ignited without any fear of a small portion of the sulphate of baryta being reduced by the charcoal of the paper.<sup>1</sup> It is necessary that the liquor from which baryta is precipitated should be warmed before or after the addition of sulphuric acid, and it should not be filtered before the precipitate has completely settled and the liquor has become perfectly clear. The clear supernatant liquor is then first poured off or decanted in a filter until only a small quantity is floating above the precipitate. Some hot water is then added, the whole is well shaken, and the sulphate of baryta is again suffered to subside completely, which operation is repeated two or three times. If this precaution be neglected,

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<sup>1</sup> Yet in doing this, it is necessary to exclude the access of air, since a portion might thus be converted into sulphuret of barium.—Ed.

the sulphate of baryta generally traverses the filter as a milky liquid.'

The quantity of baryta may also be determined as CARBONATE OF BARYTA, but as carbonate of baryta is not completely insoluble in water, this method, on that account, is not very exact, and is therefore much inferior to the preceding one. When, however, the operator is obliged to resort to it,<sup>1</sup> the baryta is precipitated from the liquor by pouring into it a solution of carbonate of ammonia. But as the common carbonate of ammonia often contains bicarbonate of ammonia, which would produce a carbonate of baryta more soluble in water, a little pure ammonia must be first added to the solution of the carbonate of ammonia, and the whole is heated in a sand bath. The carbonate of baryta obtained is washed with a small quantity of water, for although insoluble in water which contains salts in solution, it is slightly soluble in pure water. It is then dried, ignited, and weighed. It does not lose any carbonic acid by ignition.

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<sup>1</sup> This annoying condition of the sulphate of baryta has been observed by Berzelius to take place generally when it is precipitated from a neutral solution, having a certain degree of concentration; but it never takes place if the solution be either very dilute, or acid, or very concentrated. The presence of a soda-salt contributes much to this inconvenient state of the precipitate, which, once acquired, cannot be remedied either by adding an acid, nor by evaporating that solution to dryness, and treating the mass by water. It is true that the addition of an acid agglomerates the precipitate, but as soon as the operator begins to wash it, it again passes through the filter. M. Graeger says, that sulphate of baryta may be prevented from passing through the filter in the following way:—The precipitate of sulphate of baryta produced by sulphuric acid or the solution of a sulphate, is allowed to settle well at the bottom of the glass, the supernatant water is decanted and replaced by a fresh quantity of water, and again decanted. Concentrated alcohol must now be poured on the precipitate; the whole is stirred or shaken and thrown upon a filter previously moistened with weak alcohol. The alcoholic liquor passes clear through the filter, and the washing may afterwards be continued with water without fear of its passing milky.—Ed.

<sup>2</sup> This is the case in analysis in which the presence of sulphuric acid would interfere, such as in some alkaline minerals, though carbonate of baryta being only very sparingly soluble in water, much loss need not be apprehended on that account. Berzelius says, that 1 part of carbonate of baryta requires 4300 parts of cold, and 2300 of boiling water for its solution, and that it is altogether insoluble in a liquor containing a salt in solution. Dr. Fresenius, however, asserts, from the direct experiments which he undertook to this effect, that one part of carbonate of baryta requires 14,137 parts of cold, and 15,421 parts of boiling water. If the water be mixed with a little ammonia and excess of carbonate of ammonia, it is so insoluble that one part of carbonate of baryta requires 141,000 parts of the liquid.—Ed.

## SEPARATION OF BARYTA FROM THE ALKALIES.

For the purpose of separating baryta from the alkalies with which it may exist in solution, the compound is first dissolved in water, or in dilute acid, and preferably in muriatic acid, if the compound be insoluble in that menstruum; the baryta is then precipitated from the solution by pouring an excess of sulphuric acid into it; the liquor is filtered, evaporated to dryness, and the quantity of the sulphates of alkalies is determined by the processes which have been described before, (page 2).<sup>1</sup>

\* In evaporating the liquor filtered from the sulphate of baryta produced, it is necessary to operate with care towards the end, that is, when the free sulphuric acid is evaporated from the sulphate of alkali, else some portion of it might be lost. It is advisable, therefore, not to use too much sulphuric acid for precipitating the baryta in the first instance. Moreover, when the evaporation of the liquor filtered from the sulphate of baryta is so far advanced that the free sulphuric acid begins to volatilise in thick white fumes, the fire must be very carefully attended to, otherwise a loss might be produced by projection. After the expulsion of the free sulphuric acid, a small piece of carbonate of ammonia is added as before said, (page 3).

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<sup>1</sup> Sulphuric acid must be added not only in sufficient quantity to precipitate the whole of the baryta, but also to convert the alkalies into sulphates, taking care, however, not to add too much sulphuric acid.—ED.

## CHAPTER V.

## STRONTIUM.



## DETERMINATION OF STRONTIUM AND OF STRONTIA.

STRONTIA is less easily precipitated in a complete manner by sulphuric acid than baryta, because sulphate of strontia is not so completely insoluble in water as sulphate of baryta. Yet when sulphuric acid is added to the solution of a combination of strontia with an acid, which is soluble in weak alcohol, this salt may be estimated very accurately by pouring strong alcohol in the alcoholic liquor and washing the sulphate of strontia with weak alcohol, because sulphate of strontia is not soluble in dilute alcohol.

In many cases, however, the operator is compelled to precipitate strontia by pouring sulphuric acid in aqueous solutions. Such is the case when the liquor contains, besides sulphate of strontia, salts which are not soluble in weak alcohol. Although the quantity of strontia cannot then be determined with as much accuracy as that of baryta, yet this process is preferable to that which consists in precipitating strontia by means of a solution of carbonate of ammonia, because carbonate of strontia is not absolutely insoluble in water. If, however, the latter method were resorted to, an excess of carbonate of ammonia, mixed with a little pure ammonia, should be added to the liquor, and the whole heated upon a sand bath, the carbonate of strontia thereby obtained should then be filtered, washed, and ignited. It does not lose any carbonic acid by ignition.



If the strontia, the quantity of which has to be estimated, exists in a solution which does not contain any other bases, the best is to follow the same process as for the alkalies. If the liquor contains ammoniacal salts, they may be eliminated by igniting the salts of strontia.

#### SEPARATION OF STRONTIA FROM BARYTA.

Strontia is often separated from baryta by converting these two bases into metallic chlorides—igniting these salts, and, after having determined their weight, treating them by anhydrous alcohol in which chloride of strontium is soluble. As, however, chloride of strontium is not very soluble in this menstruum<sup>1</sup>, and as, on the other hand, anhydrous chloride of barium is not altogether insoluble in absolute alcohol, this method cannot be confidently depended upon, wherefore Berzelius has proposed the following:—The two earths are first to be dissolved in an excess of muriatic acid, or in acetic acid, and hydrofluosilicic acid is added, by which means the baryta is precipitated<sup>2</sup>; the strontia remains dissolved in the free acid in the state of silico-fluoride of strontium. The precipitate of silicofluoride of barium is not formed immediately, but after a certain time it settles in the form of small microscopic crystals. It is washed, collected on a weighed filter, dried, and from its weight the quantity of baryta is calculated.<sup>3</sup> Sulphuric acid is next poured into the liquor filtered from the above precipitate, and it is evaporated to dryness<sup>4</sup>. The

<sup>1</sup> According to Berzelius, 24 parts of anhydrous alcohol at the ordinary temperature, and 19 parts of boiling alcohol, dissolve 1 of chloride of strontium. Alcohol of spec. gr. 0.833 dissolves one-sixth of its weight, anhydrous alcohol dissolves only  $\frac{1}{100}$  of its weight of chloride of barium.—Ed.

<sup>2</sup> The hydrofluosilicic acid added must be in excess, and the whole left at rest for several hours, in order to allow time for the formation of the fluoride of silicium and barium.—Ed.

<sup>3</sup> The heat employed to dry this precipitate of fluoride of silicium and barium must be very moderate; in fact, the heat of a steam bath is sufficient for that purpose; for this salt, which contains no water of crystallisation, is easily decomposed by a red heat, and is transformed into fluosilicic acid gas and fluoride of barium.—Ed.

<sup>4</sup> Sulphuric acid must be added in sufficient quantity to convert the whole of

dried mass, which consists of sulphate of strontia, is ignited, weighed, and from its weight the quantity of strontia is calculated.

\* Smith has indicated *another method* of separating baryta from strontia, which is founded on the difference of solubility of the **CHROMATES** of these two earths. Their neutral solution is first diluted with a large quantity of water and a solution of neutral *chromate of potash* is added thereto ; after a little time the precipitate of chromate of baryta formed is collected on a filter without heating the whole. It is difficult to determine the quantity of strontia which exists in the filtered liquid, owing to which, Berzelius' method should be preferred.

#### SEPARATION OF STRONTIA FROM THE ALKALIES.

Strontia may be separated from the alkalies by precipitating it either in the state of *sulphate*, by means of sulphuric acid, or in the state of *carbonate*, by means of carbonate of ammonia. In both cases, the precipitate is washed, dried, gently ignited, and weighed. The whole of the alkali is then contained in the liquor filtered therefrom. If sulphuric acid has been employed to precipitate the strontia, the liquor is to be evaporated to dryness, with the precautions indicated (page 18) for the separation of baryta from the alkalies, and the dried mass is ignited with a little carbonate of ammonia, by which means the alkali is obtained in the state of neutral sulphate, (page 3). When carbonate of ammonia has been employed to precipitate strontia, the liquor is filtered, evaporated to dryness, and the dry mass is ignited. The ammoniacal salts are thereby volatilised, and the alkali remains combined with the acid with which the strontia was united before its precipitation, provided always that the acid is of such a nature as not to be destroyed by the action of

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the strontia into sulphate, for which purpose a slight excess must be added and cautiously evaporated, so as to leave the mass in a thoroughly dry state before ignition.—Ed.

operator may at once employ a neutral solution of oxalate of ammonia. The precipitate, which is oxalate of lime, takes a long time to settle, and passes through the filter if care has not been taken to warm it, and so give the precipitate a sufficient time to settle completely before filtering. In fact, the same precautions should be observed as for sulphate of baryta (page 17). In general the operator should not be in a hurry about filtering it, because oxalate of lime requires a pretty long time to precipitate completely. It is advisable, therefore before filtering the liquor, to allow it to remain at rest for twelve hours or more in a warm place. Oxalate of lime is insoluble in water, but it is soluble in acids and even in oxalic acid, wherefore it is necessary to take care that the liquor, after the precipitation, is slightly alkaline, or at least neutral.

The precipitated oxalate of lime must be well washed, dried, and ignited in a platinum crucible. During this operation the oxalate burns with a blue flame, which is due to the production of oxyde of carbon: the mass assumes a greyish tinge, but becomes almost white again under the influence of a stronger heat. The oxalate of lime, which could not be safely weighed as such, is thereby converted into carbonate of lime, which will not have lost any carbonic acid, if the heat employed has not been too strong. But as it may very well happen that the heat will have been intense enough to disengage some carbonic acid, which in most cases is caused by the action of the charcoal of the filter, the carbonate of lime should be weighed after ignition, and then uniformly moistened in the platinum crucible with a few drops of a concentrated solution of carbonate of ammonia, dried and again weighed after a gentle ignition. If the two weighings agree, no carbonic acid had been disengaged during the first ignition; if at the second weighing an increase of weight is observed, it is very probable that this excess results from the carbonic acid which has been added from the decomposition of the carbonate of ammonia.

\* Yet the increase may result also from the water of the solution of the carbonate of ammonia, which, if the operation has been performed rapidly, may not have had time to be completely expelled by the dull red heat to which it has been exposed. Wherefore it is always well to heat the carbonate of lime a second time, and then to weigh it. If the second and the third weighing agree, the operator may feel certain that he has the exact weight of the carbonate of lime. From the carbonate of lime thus obtained, the weight of the lime may be calculated.

*Another method* of precipitating lime is the following:—Carbonate of ammonia is to be added to the dilute solution of this earth, by which means a precipitate of *carbonate of lime* is formed. The solution of carbonate of ammonia employed for this purpose should first be mixed with a little pure ammonia. After the precipitation the whole is left to digest for a pretty long time in a warm place, and the filtering must not be begun before the precipitate has completely settled. After having dried the carbonate of lime thus obtained, it must be very gently ignited, or only strongly warmed, to free it from all moisture, and it is then weighed.

\* This method is not so good as the preceding one, namely, by precipitating the lime in the state of an oxalate, for oxalate of lime is much more insoluble in water than the carbonate, which, however, does not dissolve in water that contains salts, but which is slightly soluble in pure water.

The two last methods, however, are not applicable when the lime is united to phosphoric or any other acid with which it forms compounds insoluble in water, but which can be held in solution in an acid liquor.<sup>1</sup>

\* Ordinarily, in such cases, the lime is precipitated by means

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<sup>1</sup> For example, the lime from phosphate of lime cannot be precipitated by either of these two methods; for, on neutralizing the acid liquor which may hold this salt, the lime would at once be precipitated, not as lime, but as a phosphate of lime; that is to say, in the very state in which it exists in the acid solution.—Ed.

of sulphuric acid in the state of sulphate of lime, but alcohol must be added to the liquor to render the precipitate altogether insoluble in it.<sup>1</sup>

#### SEPARATION OF LIME FROM STRONTIA.

According to Stromeyer, the following method may be adopted to separate lime from strontia. The two earths are first precipitated as carbonates, which should be well washed; a little water is next poured upon the precipitate, and nitric acid is gradually added in sufficient quantity to dissolve it. But in order to obtain a solution as neutral as possible, which is absolutely necessary, the nitric acid must be added towards the end with extreme caution, and even when very near the point of saturation, it is advisable to warm the liquor before pouring a fresh quantity of acid; for when the liquor approaches the neutralizing point, and is not very dilute, the earths can no longer dissolve in the cold, so as to give a perfectly neutral solution. The liquor is next evaporated to dryness in a bottle, which can be well closed, and as soon as the residuum is dry, the bottle is immediately closed up. When the saline mass has cooled, about twice its bulk of absolute alcohol is poured upon it; the bottle is immediately closed up again, and it is frequently shaken, but the application of heat must be carefully avoided. The nitrate of lime formed, dissolves in the alcohol, whilst the nitrate of strontia remains insoluble. When the latter salt has completely settled at the bottom of the flask, the liquor is thrown on a weighed filter,<sup>2</sup> and the nitrate of strontia is washed with absolute alcohol, but the funnel should be cautiously covered with a glass plate during filtration, in order to prevent absorption of moisture. The filter with the nitrate of strontia is then dried, and from its weight the quantity of strontia is calculated. For greater certainty, dissolve the nitrate of strontia in water, pour a little sulphuric acid in the liquor, evaporate it to dryness, ignite the dry mass in a counterpoised platinum crucible, and weigh the

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<sup>1</sup> The quantity of alcohol added should be about twice the bulk of the liquid.—Ed.

<sup>2</sup> See the note, p. 5.

residuum. From the weight of the sulphate of strontia thus obtained, the quantity of the strontia may be estimated by calculation.

As to the alcoholic liquor filtered from the nitrate of strontia, and which contains the nitrate of lime, it is to be diluted with water, and heated moderately upon the sand bath until all the alcohol has evaporated; the lime may then be precipitated by oxalate of ammonia. The oxalate of lime obtained is next treated as we have said before. Yet a shorter and simpler way consists in treating the alcoholic liquor, filtered from the nitrate of strontia, by sulphuric acid, and washing the precipitate of sulphate of lime produced with dilute alcohol.

#### SEPARATION OF LIME FROM BARYTA.

Two methods may be employed for separating lime from baryta. The first consists in converting both these earths into metallic chlorides. When they are in the state of carbonates, they are supersaturated with muriatic acid, and the liquor is evaporated to dryness. The dry mass is moderately ignited in a counterpoised platinum crucible, sheltering it as much as possible from the contact of the air, and then it is weighed. If the liquor which holds the metallic chlorides in solution contains muriate of ammonia besides, which is very often the case, this latter salt would volatilise during the ignition of the dry mass. The weighed metallic chlorides are put in a flask susceptible of being well closed, and treated therein by absolute alcohol, which dissolves the chloride of calcium, only leaving the chloride of barium undissolved. The alcoholic solution is now filtered to separate the chloride of calcium from the chloride of barium, which remains on the filter, on which it is washed with absolute alcohol, the filtered liquid is then diluted with water, gently heated until the whole of the alcohol has volatilised; the lime may then be precipitated by oxalate of ammonia, and the oxalate of lime produced is treated in the manner described before.

*A simpler way* consists in precipitating the lime from the

alcoholic solution by means of sulphuric acid, and washing the precipitated sulphate of lime with aqueous alcohol.

As to the chloride of barium, which is insoluble in alcohol, it is to be dissolved in water, and sulphuric acid is poured in the solution to precipitate it as sulphate of baryta.

\* In igniting chloride of calcium the operator must see that it is done out of the contact of the air, for otherwise a portion is transformed into pure lime and carbonate of lime; wherefore it is advisable, before treating these ignited chlorides by alcohol, to pour a few drops of muriatic acid upon them.

This method, however carefully performed, does not give a very accurate result, because chloride of barium, even when freed from its water of crystallisation, is not totally insoluble in absolute alcohol<sup>1</sup>. But there is another method for separating lime from baryta, which gives a more accurate result, and which is so much the more to be preferred that, when employed, it does not signify in what acids the two earths are dissolved, or whether any alkaline salts are present or not.

This *second method* consists in diluting the liquor into which the two earths are dissolved, with a large quantity of water, then pouring sulphuric acid<sup>2</sup> therein so long as a precipitate continues to be produced. Sulphate of baryta is thrown down, and the sulphate of lime, which is not insoluble, but only sparingly soluble in water, remains dissolved, provided the liquor has been diluted with a sufficient quantity of water. After having warmed the liquor, and allowed a sufficient time for the precipitate to settle completely, it (the precipitate) is collected on a filter and carefully washed with water. When the quantity of the sulphate of lime in the precipitate is abundant, the washing must be continued for a long time on account of its sparing solubility. It is hardly necessary

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<sup>1</sup> According to Berzelius, about 400 parts of absolute alcohol dissolve 1 of chloride of barium.

<sup>2</sup> The sulphuric acid employed must also be very diluted, since otherwise sulphate of lime, which requires a large quantity of water for its solution, might be precipitated along with the sulphate of baryta.—ED.

to employ hot water for the washing, for sulphate of lime is not more soluble in hot than in cold water.<sup>1</sup> After having well washed the sulphate of baryta, its weight may be determined; this done, the filtered liquor must be saturated with ammonia, and the lime may be precipitated by oxalate of ammonia; the oxalate of lime thus produced is then treated as we have already said.

When this method is employed to separate baryta from lime, the liquor from which the baryta is precipitated by sulphuric acid, may be acid, because sulphate of baryta is insoluble in all dilute acids, but it should contain no free ammonia, because, otherwise, the solution of sulphate of lime, exposed to the air, would deposit a little carbonate of lime on the sides of the vessel, which circumstance might cause an error in the weight of the sulphate of baryta, making it appear greater than it really is, supposing that it should not have yet been filtered from the solution of sulphate of lime. Therefore, when such a solution contains free ammonia it should be first supersaturated with an acid.

#### SEPARATION OF LIME FROM STRONTIA AND BARYTA.

When lime has to be separated from baryta and strontia, the process is as follows:—The three earths should be precipitated together in the state of carbonate by means of carbonate of ammonia, mixed with a little pure ammonia, taking care to warm the liquor. The carbonates are then dissolved in muriatic acid, the solution is evaporated to dryness, the dry mass is ignited, and then treated by absolute alcohol, which leaves the chloride of barium untouched, but which dissolves the chloride of strontium and of calcium. The alcoholic solution is then mixed with water, and the alcohol is evaporated by a gentle heat, after which, nitric acid being poured in the liquor, it is to be

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<sup>1</sup> By using hot water, however, the filtering proceeds with much greater rapidity, a circumstance of some moment, when the precipitate has, like the present, to undergo protracted washing, my filtering apparatus described page 33, will be found advantageous.—Ed.



evaporated to dryness, by which means, the chlorides are converted into nitrates, which may then be treated as we have said before.

It is better, however, first to precipitate the baryta from the liquor which holds the three earths in solution, by means of hydrofluosilicic acid, filtering, and adding sulphuric acid to the filtered liquor, evaporating to dryness, igniting the dry mass, by which means sulphate of strontia and sulphate of lime are obtained. These two salts are now mixed in a platinum crucible, with three times their weight of carbonate of soda or of potash, the whole is fused, water is poured upon this fused mass, and an insoluble compound is obtained, which is composed of carbonate of strontia and of carbonate of lime. These two earths may then be separated from each other as we have said, (page 27).

#### SEPARATION OF LIME FROM THE FIXED ALKALIES.

It is very easy to separate lime from the fixed alkalies. The lime is precipitated from the liquor by oxalate of ammonia, and the liquor filtered from the oxalate of lime produced is evaporated to dryness; the dry mass is ignited in a counterpoised platinum crucible, and weighed. The fixed alkali combined with the acid to which it was united in the liquor is thus obtained, provided always that the alkaline salt is one which is not decomposable by heat. If, for example, the lime and the alkali were dissolved in muriatic acid, chloride of potassium, chloride of sodium, &c., would be obtained—the ammoniacal salts which were in solution in the liquor, as, for example, the excess of oxalate of ammonia, or muriate of ammonia, would be destroyed or volatilised by the heat.

It is necessary, however, to operate with the utmost care when the lime has been precipitated by oxalate of ammonia from a liquor which contained sulphuric acid, or sulphate of ammonia. If the quantity of sulphate of ammonia be considerable, it is difficult to guard against a loss. Sulphate of ammonia fuses and is decomposed with projection before

volatilising. It is advisable to evaporate the liquor filtered from the oxalate of lime in a somewhat large platinum capsula, and to ignite the dry mass in this capsula until all the ammoniacal salts are eliminated. The sulphate of alkali obtained is then poured in a small counterpoised platinum capsula or crucible; the larger capsula is washed with water, and the washing is put also in the small capsula; the whole is then evaporated to dryness, and, after ignition, the residuum is weighed. Pending the ignition, it is necessary, in order to expel the excess of sulphuric acid completely, to use a little carbonate of ammonia, as we have already said, (page 3).

## CHAPTER VII.

## MAGNESIUM.

## DETERMINATION OF MAGNESIUM AND OF MAGNESIA.

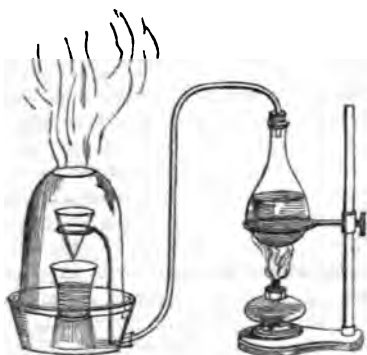
THE quantitative estimation of magnesia is often attended with numerous difficulties. The quantity of this earth, in many cases, cannot be determined with as much precision as that of the substances of which we have been hitherto speaking.

If magnesia exists in a liquor from which no other substance has to be quantitatively separated, and if the liquor contain no other fixed constituent, it is evaporated to dryness; the mass is ignited in a counterpoised platinum crucible, by which means the ammoniacal salts, if any be present, are volatilised. Sulphuric acid, diluted with a little water, is then carefully poured on the ignited mass; the whole is evaporated to dryness, and the residuum is slightly ignited in order to expel the excess of sulphuric acid. The residuum is weighed; it consists of neutral sulphate of magnesia, from the weight of which the quantity of the magnesia may be calculated. If the liquor at first contained sulphuric acid, it is clear that the dry mass need not be supersaturated with sulphuric acid after the first ignition; but when the liquor contains ammoniacal salts, sulphuric acid should be added only after the volatilisation of these salts, because sulphate of ammonia would otherwise be formed, which cannot be easily volatilised without losing some of the residuum, because it then begins to fuse, and spirts out very much.

But when the liquor contains, besides magnesia, other fixed constituents, as, for example, salts of potash, and magnesia alone is required to be quantitatively determined, it may be precipitated as carbonate of magnesia by means of a solution of carbonate of potash; but as neutral carbonate of magnesia, which should be precipitated by the neutral carbonate of potash added, is decomposed by water, the result of which is to produce bicarbonate of magnesia which is soluble in this liquid, the operator must, in order to avoid this obstacle, boil for a long time the magnesian solution with an excess of carbonate of potash. The best is to employ for the purpose a platinum capsula as large as possible. The precipitated carbonate of magnesia is collected on a filter, and washed with hot water. It is necessary to be careful not to interrupt the washing or to continue it for too long a time, because carbonate of magnesia is not absolutely insoluble in water, though it is less soluble in hot than in cold water; so that water as hot as possible must be employed to wash it.<sup>1</sup> Having continued the washing so long that a few drops of the washing being evaporated on a strip of platinum foil, leave only a slight pellicle, the precipitate is dried, ignited,

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<sup>1</sup> For the purpose of filtering rapidly, I contrived the following apparatus, which consists of a common Florence flask, two-thirds full of water, connected by a pewter or tin pipe with a dish, having a circular rim inside, on which a large glass beaker,



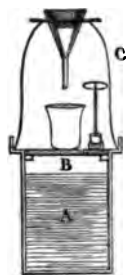
from which the bottom has been removed, or a glass bell open at top is placed mouth downwards; a small support, which may be an inverted crucible, receives the beaker

and weighed. The action of the fire expels the carbonic acid, and therefore the ignition must not be discontinued too soon.

\* Considering, however, that if the boiling has not been long enough, some magnesia might still remain in solution, it is advisable, after boiling, to take the liquor filtered from the carbonate of magnesia, to put it in a porcelain capsula, or, better still, in one of platinum, to evaporate it to dryness by a strong heat, taking care, in order to avoid the loss which might be incurred by projection, to stir the mass incessantly, especially towards the end. The dry residuum is then washed with boiling water, which often leaves a small residuum of carbonate of magnesia, which being collected on a filter, must be washed with hot water.

\* But as the liquor filtered from the carbonate of magnesia precipitated by boiling, ordinarily contains as yet a little carbonate of magnesia mixed with the excess of carbonate of alkali, owing to which the operator is obliged to evaporate it to dryness, it is not necessary to filter all the liquor after the ebullition; it suffices to allow the carbonate of magnesia to settle at the bottom, and to decant the hot supernatant liquor ;

into which the filtered liquid falls from the paper filter held by a platinum ring, adjusted at a convenient height, and in a convenient position, by bending the platinum wire terminated by the ring. A lighted spirit-lamp being now put under the Florence flask generates steam, which, passing through the tin pipe, soon fills up the whole apparatus, and escapes through the bottomless inverted beaker. By this contrivance not only the filtering proceeds rapidly, but whilst taking place the precipitate, being in an atmosphere of steam, is sheltered from the action of the air. This filtering apparatus may be modified as follows : A is a reservoir of water, which may be placed over a lamp, or upon a stove, so as to generate the steam. B is a cullender, resting upon a circular rim, and through the holes of which the steam of the water below escapes : this cullender has a little socket for receiving a cork, and in the cork a stout platinum wire is thrust, which is terminated by a ring for supporting the filter, or else it may be turned on one side, and the filter may be placed either alone, or in a funnel, in a porcelain support, placed over the perforated glass beaker C, which forms the steam chamber. It must be borne in mind, that though filtering and washing is considerably accelerated by this apparatus, yet there are sometimes particular reasons for avoiding the use of hot water.—Ed.



hot water is then poured upon the precipitate collected on a filter; it is washed, and both the decanted liquor and the washings are together rapidly evaporated to dryness.

When magnesia is to be precipitated by carbonate of potash, several precautions must be observed, which, if neglected, may be the cause of very serious errors, and very inaccurate results.

\* First of all, especial care must be taken for the purpose of evaporating the liquor to dryness, to employ, not a gentle heat, but as much as possible a boiling temperature. It is true that in acting thus it is difficult to avoid a slight spirting, but on the other hand, the operator has not to fear any loss from the efflorescence of the salts, which hardly ever takes place except when a gentle heat is applied to evaporate a saline liquor; added to which, a very sparingly soluble combination of carbonate of magnesia and of carbonate of potash is formed under the influence of a gentle heat, which considerably augments the apparent weight of the carbonate of magnesia, though a great quantity of the combination is dissolved during the washing. This combination is decomposed by a red heat, which deprives the magnesia of its carbonic acid, so that, upon treating the ignited mass with water, the carbonate of potash is dissolved, and the magnesia remains insoluble. Therefore, it is always necessary, after igniting, to treat the ignited magnesia with water, in order to see whether it is pure, and whether the water dissolves much carbonate of potash; if so, the magnesia must be washed with hot water, ignited again, and weighed.

\* If the presence of potash has been ascertained in the magnesia, it is necessary, after having weighed the latter, to dissolve it in dilute muriatic acid. If the magnesia has been precipitated by carbonate of potash, there generally remains, after dissolving it in the acid, a small quantity of silicic acid which is collected on a filter, washed, ignited, and weighed, and the weight of which being deducted from that of the magnesia, gives the exact quantity of the latter. This silicic acid comes, in most cases, from the carbonate of potash employed, for it is extremely difficult to obtain it perfectly free from that substance.

When the liquor which contains magnesia, contains also considerable quantities of muriate or other salts of ammonia, the ammoniacal salts must be decomposed before the magnesia can be totally precipitated by carbonate of potash, and, to effect this, an excess of carbonate of potash must be added, the whole heated for a long time, until the ammoniacal salts are decomposed, and then boiled for some time. Those, however, who have not yet acquired sufficient practice often commit a mistake in reference to the quantity of carbonate of potash which should be used. In order to ascertain whether enough carbonate of potash has been employed, the liquor must be heated until it smells no longer of ammonia, and then a little more carbonate of potash is added; if the heat gives rise to a fresh disengagement of an ammoniacal odour, it is a proof that the carbonate of potash added is not as yet in sufficient quantity. The operator continues to do this until the last quantity of carbonate of potash added exhales no further odour of ammonia. After having separated the carbonate of magnesia by filtering, and evaporated the filtered liquor to dryness, the water with which this dry residuum is washed should impart a strong blue colour to reddened litmus paper. If the colour of the paper does not change, it is a proof that the quantity of carbonate of potash employed was not sufficient to decompose the ammoniacal salts, and that another portion of carbonate of potash must be added to separate all the magnesia from the liquor.

\* Formerly when after the addition of carbonate of potash the magnesia had been precipitated by boiling, the whole was evaporated to dryness without separating the latter. Water was poured upon the dry mass, and the undissolved carbonate of magnesia was collected on a filter. According to Bonsdorf, this method is not so good as that which we have just described. In effect, it appears that the double carbonate of magnesia and potash, of which we have spoken above, may be formed also at a certain temperature, during the drying of the mass, by the reaction of the excess of carbonate of potash upon the precipitated carbonate of magnesia.

In all cases pure potash, which precipitates magnesia even better than carbonate of potash, may be employed instead of the latter substance, but then the precipitate consists of pure magnesia, which is more soluble in water than its carbonate, although it is like this last body, less soluble in boiling than in cold water.

Carbonate of soda may be employed instead of carbonate of potash, and with the same result. It is true that Mosander has asserted that this salt is not appropriate to the quantitative estimation of magnesia, because it forms with carbonate of magnesia a double salt which is not decomposed by boiling, and which is still more soluble in water than the corresponding double salt of potash.

\* But Bonsdorf has shown since, that when the precautions, which have been related above are observed, carbonate of soda precipitates magnesia quite as completely as carbonate of potash. It cannot be denied, however, that these precautions must be observed with still greater care, because carbonate of soda is more liable than carbonate of potash to form a sparingly soluble salt with carbonate of magnesia. Carbonate of soda has, however, this great advantage, that being always free from silicic acid, none can be mixed with the precipitated magnesia, owing to which, when it has been precipitated by carbonate of soda, it dissolves, after ignition, without residuum, in muriatic acid, even when extracted from substances which contain silica.

*A second method* for precipitating magnesia from its solutions, is by a solution of phosphate of soda, with addition of ammonia. Either pure ammonia or its carbonate may be used. After precipitation, the whole is left in a warm place for a long time, that is, twelve hours at least. A deposit of bibasic phosphate of ammonia and magnesia [ $2 \text{ MgO}$ ,  $\text{NH}_4\text{O}$ ,  $\text{PO}_4$ , +12 aq.] is formed, which requires a rather long time to settle under the form of a crystalline precipitate.

\* This precipitate, although long to form, is totally insoluble in a liquor which holds phosphate of soda in solution, but it is



not insoluble in pure water. It should not, therefore, be washed too long, otherwise the water of the washing becomes turbid when mixed with the liquor, which has percolated first, and which contains phosphate of soda<sup>1</sup>. Practice alone can teach when the precipitate has been sufficiently washed. After having dried it, it is ignited, by which operation the water and ammonia are expelled; the residuum is a neutral phosphate of magnesia only. During ignition the precipitate deflagrates. The quantity of magnesia contained in the phosphate of magnesia may then be calculated by means of the tables<sup>2</sup>.

\* When great accuracy is required, however, it is better to precipitate magnesia by carbonate of alkali instead of by a solution of phosphate of soda, with addition of ammonia, because the precipitate of the bibasic phosphate of ammonia and magnesia is somewhat soluble. When a speedy result is desirable, it is preferable to use the latter method, which is conveniently employed also when the liquor under examination contains a great quantity of ammoniacal salts, and only very little magnesia.

\* When magnesia has been precipitated from a liquor by means of a solution of carbonate of potash, or of soda, observing the precautions which we have related above; the operator, after having washed the precipitate, instead of evaporating to dryness the filtered liquid with the excess of carbonate of alkali, may precipitate the small quantity of magnesia which it retains

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<sup>1</sup> The formula of this neutral phosphate is  $2 \text{ Mg. O, PO}_3$ , and it contains 36.67 per cent. of magnesia.—Ed.

<sup>2</sup> Dr. Fresenius has shown that it is not the presence of phosphate of alkali, but that of ammonia, which renders this precipitate insoluble, since ammonia precipitates this salt completely, even when the liquor no longer contains any phosphate in solution; so that the precipitate may be washed with water, rendered alkaline by ammonia. Dr. Fresenius has determined, by experiment, that one part of this basic phosphate of magnesia and ammonia dissolves in 15293 parts of pure water, and that this cold saturated solution being treated by ammonia, produced, after some time, a perceptible crystalline precipitate, whilst the addition of phosphate of soda left the solution perfectly clear. It has been estimated that one part of the bibasic double phosphate in question requires for solution 45000 parts of water, rendered ammoniacal; which, therefore, may be used to wash the precipitate thoroughly without sensible loss.—Ed.

by pouring a solution of phosphate of soda into it, and then adding ammonia. The advantage of this method is to avoid the necessity of evaporating the liquor to dryness. That which, however, stands in the way of this method being always resorted to is, that the liquor, if sufficient care has not been taken, might often contain a considerable quantity of magnesia, which would then be determined less accurately in the state of ammonio-phosphate of magnesia, than as carbonate of magnesia. But those who are not used to analytical operations, must always, when they think they have precipitated all the magnesia from a liquor by means of carbonate of potash, test this liquor by a solution of phosphate of soda, with addition of ammonia, before rejecting it.

As it is already very difficult to determine exactly the quantity of magnesia when it exists alone in a liquor, the difficulties increase very much when it has to be quantitatively separated from other substances.

#### SEPARATION OF MAGNESIA FROM LIME.

When a liquor contains both lime and magnesia, several methods may be resorted to for the purpose of separating these two earths; but the following are more generally employed:—

If the liquor containing *lime* and *magnesia* contains also muriate, or other salts of ammonia, which is very often the case, it is suitably diluted with water, and a very slight excess of pure ammonia is added. When it contains no ammoniacal salts, a solution of muriate of ammonia is poured into it. If, however, the liquor is acid, this addition of muriate of ammonia need not be made, because, in saturating it with ammonia, there will be a sufficient quantity of salt of ammonia formed. Ammonia produces no precipitate in magnesian solutions, when it contains enough of a salt of ammonia. If a precipitate be produced owing to a deficiency of an ammoniacal salt, the precipitate is to be dissolved by acid, for example, by muriatic acid, and the liquor must again be saturated by ammonia, the addition of which no longer determines any precipitate. This

done, the lime is precipitated from the liquor by oxalic acid, or by oxalate of ammonia, as we have said (page 24.) The magnesia is not precipitated thereby, owing to the presence of the ammoniacal salts, though oxalate of magnesia itself is almost insoluble in water. After having separated, by filtering, the oxalate of lime produced, the magnesia may be separated from the filtered liquor by carbonate of potash, or of soda, as we have said before.

*Another method* indicated by R. Phillips and Cooper, is the following :—When the liquid under examination, besides lime and magnesia, contains other fixed constituents, as, for example, alkalies, the two earths are precipitated by carbonate of potash or of soda, water is poured upon the dry mass, and the earthy carbonates are washed with boiling water. They are then cautiously supersaturated with dilute sulphuric acid, the whole is evaporated to dryness, and the dry residuum is ignited in a counterpoised platinum crucible in order to expel completely the excess of sulphuric acid. If, on the contrary, the solution contains no other fixed constituents besides lime and magnesia, and if these earths exist therein, in combination with acids which can be expelled by sulphuric acid, it is evaporated to dryness, the dry residuum is ignited when it contains ammoniacal salts, in order to volatilise them, it is then treated by sulphuric acid, and it is again ignited to expel the excess of sulphuric acid. The ignited mass is weighed and digested with a saturated solution of sulphate of lime. This solution dissolves the sulphate of magnesia only, and leaves the sulphate of lime which is to be washed with a saturated solution of sulphate of lime so long as the operator thinks that it retains any sulphate of magnesia. This done, the remaining sulphate of lime is ignited,<sup>1</sup> and weighed. The difference of weight indicates the quantity of sulphate of magnesia, and from the weight of the

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<sup>1</sup> Before igniting the filter which contains the sulphate of lime, it should be gently pressed between folds of blotting paper, so as to remove the moisture of the filter as much as possible, in order to reduce the increase of weight on account of the solution of sulphate of lime, which the filter has imbibed.—Ed.

sulphates the quantity of the earths which they contain may be calculated. This method, which may be employed with much advantage in certain cases, is rather less certain than the one first described; the operator cannot know when the whole of the sulphate of magnesia is washed out, and even the filter on which the sulphate of lime is washed, remains saturated with a certain proportion of the solution of this salt, a circumstance which must necessarily cause a slight increase in the weight obtained. For these reasons this method is seldom resorted to.

\* *A third method* for separating magnesia and lime, consists in dissolving them both in an acid, and preferably in muriatic acid, pouring in the acid solution; first sulphuric acid, and then enough alcohol to bring the latter to the strength of weak spirits of wine.<sup>1</sup> The sulphate of lime produced, and which is completely insoluble in such a liquor, is washed with alcohol diluted with water to about the strength of brandy, which cannot precipitate sulphate of magnesia nor dissolve sulphate of lime; the liquor filtered from this precipitate is to be exposed for a long time to a gentle heat, in order to expel the alcohol, after which the magnesia may be precipitated therefrom. If the two earths were contained in a very dilute liquor, it should be concentrated by evaporation until, by adding alcohol, the liquid should have the strength of weak spirits of wine. Yet it is necessary that the liquor, after the addition of sulphuric acid, should contain no other substance insoluble in dilute alcohol, except sulphate of lime. This method is conveniently applied when the two earths which have to be separated are combined with phosphoric acid, or when the liquor in which they are dissolved contains phosphoric acid. But, in such cases, it is necessary, after having separated the sulphate of lime, and evaporated the alcohol, to precipitate the magnesia in the state of bibasic phosphate of ammonia and magnesia.

There are other methods of separating lime and magnesia,

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<sup>1</sup> This may be attained by adding to the solution about twice its bulk of alcohol.—Ed.

but which need not be mentioned here because the result which they give is less certain than the methods which we have described.

#### SEPARATION OF MAGNESIA FROM STRONTIA AND BARYTA.

The separation of magnesia from strontia and baryta presents no difficulty. If these earths be contained in a liquid, the baryta and strontia are precipitated in the state of sulphates, after which the magnesia, held in solution in the filtered liquor, may be estimated as sulphate of magnesia, or else it may be precipitated by carbonate of potash, as we have said before. Sulphate of strontia not being quite so insoluble in water as sulphate of baryta, the latter is much more easily separated from magnesia by this method than strontia.

#### SEPARATION OF MAGNESIA FROM THE FIXED ALKALIES.

The separation of magnesia from the fixed alkalies is exceedingly difficult. This earth and the alkalies must first be converted into sulphates, which is very easily accomplished.

\* If the alkali and the magnesia are dissolved in a liquid which contains no sulphuric acid, but in which ammoniacal salts are present, the solution is evaporated to dryness, the residuum is ignited until the ammoniacal salts are expelled, and the ignited mass is treated by sulphuric acid. If the sulphuric acid be added to the liquor before having expelled the ammoniacal salts, too large a quantity of sulphate of ammonia is produced, the expulsion of which, by a red heat, almost invariably determines a loss of the remaining mass by spirting. The sulphate of alkali and the sulphate of magnesia are gently ignited, in order to expel the excess of sulphuric acid. In order completely to convert the bisulphate of alkali into the neutral sulphate, the mass must subsequently be treated by a small quantity of carbonate of ammonia as we have said (page 3).

The neutral sulphates of alkali and of magnesia are weighed

and dissolved in water, a solution of acetate of baryta (which must be perfectly free from chloride of barium) is added to the solution, until the whole of the sulphuric acid is precipitated in the state of sulphate of baryta. The whole is now heated, the sulphate of baryta is separated by filtering, the filtered liquid is evaporated to dryness, and the dry mass is ignited in a platinum capsula. The acetates are thereby converted into carbonates, and the carbonate of magnesia loses its carbonic acid either partially or entirely, according to the intensity of the ignition. Hot water is now poured upon the ignited mass, whereby the carbonate of alkali is dissolved, whilst the carbonates of baryta and of magnesia remain behind. The solution of the carbonate of alkali is separated by filtering from this residuum, which must be washed with hot water; the washing must not last too long, because both the carbonate of baryta and that of magnesia are not absolutely insoluble in water. The alkaline liquor is evaporated to dryness, the dry residuum is ignited, weighed, and then converted into a metallic chloride or into a sulphate of alkali, because it is then more easily weighed.

The carbonates of baryta and of magnesia which have remained undissolved, are now dissolved in muriatic acid, and the baryta is precipitated from the solution by means of sulphuric acid, after which the sulphate of baryta precipitated is separated by filtering, and the filtered liquor is evaporated to dryness. The dry residuum is ignited and weighed; it consists entirely of sulphate of magnesia. If the weight of the sulphate of alkali be now added to that of the sulphate of magnesia, the total must be equal to that which had been obtained before the separation of the two bodies.

This method, as may be seen, is a very complicated one, and cannot give absolutely accurate results, because the carbonates of baryta and of magnesia are not quite insoluble in water.

This method, however, can be employed only for separating potash and soda from magnesia and could not be employed for the separation of lithia, because carbonate of lithia is only very sparingly soluble in water. Wherefore, when lithia alone has

to be separated from magnesia, the latter should first be precipitated by carbonate of soda, as we have said before; the precipitate is separated by filtering, and the lithia may then be precipitated from the filtered liquid in the state of double phosphate of soda and lithia, as we have already said (page 14).

\* Liebig proposed another method to separate magnesia from potash and soda. The bases are combined with sulphuric acid, the solution is rendered neutral, and it is precipitated by a solution of sulphuret of barium, which separates all the potash and all the soda from the magnesia. The alkalies remain in the liquor in the state of sulphuret of potassium, or of sodium, together with the excess of sulphuret of barium employed. This liquor is decomposed by sulphuric acid, and the sulphate of baryta produced is collected on a filter; by evaporating the liquid filtered therefrom the sulphate of alkali is obtained<sup>1</sup>. The best method of extracting the magnesia from the precipitate produced by the sulphuret of barium<sup>2</sup>, is to use an acid, and sulphuric acid in preference, to filter in order to separate the sulphate of baryta produced, and the magnesia may be determined afterwards as sulphate of magnesia.

\* The sulphuret of barium employed for this method of analysis, must be crystallised and washed with cold water, such as it is obtained from the boiling of the product of the calcination of a mixture of sulphate of baryta and of charcoal.

\* Hydrate of baryta may be substituted for sulphuret of barium with the same result.

\* The fixed alkalies may be more easily separated from magnesia when these bases are combined with nitric acid. The nitrates are to be calcined, which may be done in a platinum crucible by adding a little dry carbonate of ammonia to the mass, after exposure to the first impression of the heat, and then moderately urging the fire. When the calcining is finished, the residuum is treated by water, which dissolves the

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<sup>1</sup> The sulphates of alkali thus obtained may be weighed, and from this weight the quantity of the alkali may be calculated.—Ed.

<sup>2</sup> This precipitate consists of magnesia mixed with sulphate of baryta.—Ed.

alkalies in the state of carbonates and leaves the magnesia behind.

\* It is likewise less difficult to separate the fixed alkalies from magnesia, when these bases are combined with oxalic acid, or with another organic acid, because the salts of alkalies are then, by ignition, converted into carbonates, and may then be easily separated from magnesia by washing with water.

\* When the fixed alkalies and magnesia are contained in a solution in the state of metallic chlorides, the method formerly in use for separating them consisted in evaporating the liquor to dryness and igniting the dry residuum; the water of crystallisation of the chloride of magnesium converted the latter into magnesia, with disengagement of muriatic acid, after which the chloride of the alkalisable metal was separated from the magnesia by washing with water.

\* This method may often be employed with advantage in qualitative analysis, but in quantitative analysis the results obtained by it are quite inaccurate, for even after a protracted ignition there remains a great quantity of undecomposed chloride of magnesium, which dissolves in the water with the alkaline chloride. If strong alcohol is employed instead of water for washing the strongly ignited mass, it does not give a better result, for alcohol dissolves the undecomposed chloride of magnesium, just as water does, and leaves the magnesia thus produced undissolved.

\* Yet if, after having put the mixture of chloride of magnesium and of the alkalisable metal in a small platinum crucible, it is exposed to a red heat for a long time upon a spirit-lamp with circular wick, placing at the end a small piece of carbonate of ammonia upon the mass, and then igniting the whole strongly, nearly the whole of the chloride of magnesium may be converted into magnesia; but the calcination with the ammoniacal salt must be repeated several times, and the salt must be moistened with a few drops of water before calcining. The operation is known to be at an end when the weight of the saline mass remains constant after ignition. It is then treated by water,



which dissolves the alkaline chloride, and along with it an imponderable trace of magnesia. The magnesia which remains insoluble is ignited and weighed. It is completely soluble in nitric acid, and when tested by nitrate of silver hardly shows a trace of chlorine. During the ignition of the mass, it is advisable to put the cover on the crucible, in order to keep in the vapour of carbonate of ammonia as long as possible, and to prevent at the same time the access of air.

\* When the operation is performed on a few grammes of a mixture of chloride of magnesium, and of the chloride of an alkalisable metal, the treatment with carbonate of ammonia and water must be repeated at least eight times. The unavoidable loss of alkaline chlorine which takes place when this method is resorted to, does not amount to one per cent. Of course the chlorides, which the operator purposes to separate, must contain no trace of sulphuric acid.

\* Although chloride of potassium and of sodium are both somewhat volatile by exposure to a red heat, in the contact of the air, they are not so when kept plunged in an atmosphere of carbonate of ammonia and water, taking care to exclude the air as much as possible; and when this is done, there is no fear of losing any of the alkaline chloride from this cause.

\* But this method cannot be resorted to for separating chloride of lithium from chloride of magnesium, at least without a considerable loss; for, in treating the ignited mass by water, only ninety-three per cent. of the real quantity of chloride of lithium are obtained, because when this salt is several times ignited with carbonate of ammonia, it becomes partly converted into carbonate of lithia, which, on account of its difficult solubility cannot be accurately separated from the magnesia. The quantity of carbonate of lithia produced is much larger than when chloride of lithium alone is ignited with the contact of the air.

As chloride of calcium is still more easily altered than chloride of lithium by ignition with carbonate of ammonia, in consequence of which a rather considerable quantity of carbonate of

lime is formed, chloride of calcium cannot be separated from chloride of magnesium by this method<sup>1</sup>.

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The following note of M. E. Peligot is found in the French edition :—

\* Magnesia is separated from potash and from soda, according to Berzelius, by transforming these substances into chlorides, and adding peroxyde of mercury to their concentrated solution ; it is then evaporated to dryness and then treated by water. All the magnesia remains mixed with the excess of peroxyde of mercury only ; and on evaporating again to dryness and calcining, the alkaline chlorides remain in the pure state.

\* According to Döbereiner, lime may be separated from magnesia in the following manner :—The muriatic solution is evaporated to dryness, and the residuum is calcined in a platinum crucible until muriatic acid ceases to be disengaged ; chlorate of potash is then added until the odour of chlorine is no longer perceived ; treating now the mass by water, the chloride of calcium dissolves, and the magnesia remains in an insoluble state.

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<sup>1</sup> Another method for separating magnesia from the fixed alkalies has been proposed by Berzelius (*Jahres-bericht*, xxi., vol. ii., page 142). It consists in converting the bases into chlorides, if they are not already in that state, and mixing the concentrated solution with peroxyde of mercury, and evaporating the whole to dryness. The chloride of magnesium is thereby decomposed, and converted into pure magnesia, whilst, at the same time, perchloride of mercury is formed, which combines with the alkaline chlorides (forming with them a double salt). The dry mass is then treated by water, the solution is filtered, evaporated, and the residuum is ignited, in order to expel the chloride of mercury, and the chlorides of alkali remain in solution, from the weight of which salts the quantity of alkali may be deduced. Magnesia is left, which, as it may be mixed with oxyde of mercury, should be ignited, in order to expel the latter, after which pure magnesia remains, which may be weighed.—Ed.

## CHAPTER VIII.

## ALUMINIUM.

## DETERMINATION OF ALUMINIUM AND ALUMINA.

ALUMINA is completely precipitated from its solutions by ammonia and carbonate of ammonia. The precipitate is very bulky and difficult to wash, for which purpose boiling water is preferable. It undergoes an extraordinary contraction in drying, and it should be perfectly dry before igniting and weighing it. The ignition must be performed with great care, because dry alumina sometimes decrepitates and may occasion a loss.

Of the two re-agents just mentioned, carbonate of ammonia is the best for precipitating alumina, and it should always be employed when it is not necessary to avoid the presence of carbonic acid. Even when a neutral solution of alumina is precipitated by carbonate of ammonia, or other carbonates of alkali, an effervescence is produced by a disengagement of carbonic acid, because this acid does not combine with alumina. Pure ammonia precipitates alumina very well also, and it is resorted to in a great number of cases in which carbonate of ammonia cannot be employed; but a very great excess of it must be avoided, because traces of alumina might then be dissolved; in effect if in, such a case the precipitate being separated by filtering the filtered liquor is heated until the excess of ammonia has volatilised, an inconsiderable quantity of alumina separates in flakes, but generally these flakes are almost imponderable.

*Carbonate of potash, or of soda*, cannot be conveniently employed to precipitate alumina, for although these two salts precipitate alumina entirely, yet it is extremely difficult, and even almost impossible, to separate the last traces of potash or of soda by washing, owing to which, in weighing alumina, a somewhat greater weight is obtained than should be. When the operator is compelled to resort to carbonate of potash, or of soda, the precipitate (for very accurate quantitative analysis) must be collected on a filter, re-dissolved in an acid, for example in muriatic acid, and the earth must be reprecipitated by carbonate of ammonia. Alumina is sparingly soluble in very concentrated and boiling solutions of carbonate of potash or of soda.

\* Alumina is found in nature in such a compact state in *corundum*, that it is inattackable by acids; they cannot dissolve it even after fusion with carbonate of potash, or of soda. Several native combinations of alumina, with some bases in which the former plays the part of an acid, have a like degree of density. Such is the combination of alumina and magnesia called *spinelle*. Such bodies cannot be dissolved by acids except after fusion with pure potash, or very strong ignition with carbonate of baryta. Their decomposition by pure potash, or by baryta, requires numerous precautions. The process followed in such cases is the same as that which is employed when certain siliceous combinations are treated by pure potash or baryta, and as I shall speak of it at length when I come to treat of the quantitative determination of silicic acid, the reader is referred to that part.

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Note by Peligot in the French edition:—

M. Rose has lately shown that corundum and the aluminates reduced into fine powder, dissolve completely by fusion with bisulphate of potash, and that the fused mass dissolves without residuum in water. The pulverising must be performed in a steel mortar, and the powder sifted through a fine piece

of cambric; the powder is then fused in a platinum crucible with an excess of bisulphate of potash, by means of an argand spirit-lamp. The substance under examination must not be pulverised in an agate mortar, because it would take up some silica. Moreover, it is necessary to treat again by muriatic acid the alumina which has been precipitated by ammonia, because it has separated in the form of basic sulphate, and it must be precipitated a second time by ammonia, in order to obtain it in a pure state, and to weigh it.

#### SEPARATION OF ALUMINA FROM MAGNESIA.

There are several methods of separating alumina from magnesia. To the solution of these two earths, as much of a solution of muriate of ammonia is added as is thought sufficient to prevent the magnesia from being precipitated by the addition of pure ammonia, after which the alumina is precipitated by ammonia. If the solution of the two earths is acid, it is not necessary to add muriate of ammonia, because the saturation of the acid by ammonia produces a sufficient quantity of ammoniacal salt to retain the magnesia in solution.

The alumina is collected on a filter and washed. It is not necessary, however, to wash it in a complete manner, for it is not perfectly pure, and contains, as yet, a little magnesia. Even when a very large quantity of muriate of ammonia has been added to the liquor, a little magnesia is carried down with the alumina, and it cannot be prevented, probably by reason of the chemical affinity which alumina has for it.

\* After ignition, the precipitate obtained by ammonia can no longer be completely dissolved in muriatic acid; the alumina remains insoluble and mixed with a certain quantity of magnesia.

In order to separate this small portion of magnesia, the alumina must be treated by a solution of pure potash whilst yet moist. The best mode of doing this is to put both the moist filter and the precipitated alumina in a glass, and to dissolve it by muriatic acid, taking care, however, not to put

too great an excess of acid; the liquor is filtered, and the filter must be well washed.

To the above muriatic acid solution an excess of solution of potash is added, and the whole is heated in a porcelain capsula, or, better still, in one of platinum. The alumina is dissolved by the solution of potash whilst the small quantity of magnesia remains undissolved. The solution takes place even in the cold, but it is always better to employ heat in order to separate it more completely. The small quantity of magnesia is collected on a filter and washed; after which it is digested with the wet filter in muriatic acid, by which it is dissolved. The filter is well washed, and the solution of the small quantity of magnesia is added to that which contains the greatest proportion of this earth, and which was originally filtered from the precipitate produced by ammonia. By thus mixing the two liquors together, the whole of the magnesia is collected, and it may then be determined as we have described in the paragraph which treats of the dosing of this earth.

There still remains to determine the quantity of alumina held in solution by the caustic potash. Muriatic acid is poured in this solution in sufficient quantity to re-dissolve the alumina which has been precipitated at first, and leave a very slight excess of acid. The alumina is then precipitated from the muriatic acid solution by ammonia, or, better still, by carbonate of ammonia. This method of precipitating alumina from its solution in potash, is much preferable to another which is less expensive, which is usually employed, and which consists in pouring a solution of muriate of ammonia in the alkaline solution of alumina; the potash is thereby converted into chloride of potassium; the alumina is precipitated, and the ammonia becomes free. But the great quantity of ammonia generated may keep a small quantity of the alumina in solution, and, moreover, a little potash is carried down with the alumina, and an increase of weight is the result.

*Another method of separating alumina from magnesia consists*

in dissolving the two earths in an acid—for example, in muriatic acid, (taking care, however, to avoid putting an excess of it);—pouring in that solution an excess of one of pure potash; and by heating the whole, the alumina is dissolved, and the magnesia remains behind. But, notwithstanding the shortness of this process, it is by no means preferable to the one which we have just described, because, in presence of a large quantity of magnesia, alumina cannot be completely separated from this earth by potash. It is therefore better to begin by separating the alumina from the greatest portion of the magnesia, and then to dissolve the first of these two bases in potash. When, however, very small quantities only of magnesia have to be separated from very considerable quantities of alumina, this second method may be employed.

*A third method of separating alumina from magnesia consists in pouring a solution of bicarbonate of potash in the solution of these two earths, previously diluted with water. A strong effervescence takes place, the alumina is completely precipitated and the magnesia remains dissolved. The precipitate is washed with cold water, generally this washed precipitate is dried, then weighed, and its quantity is determined. Yet, I have already said that it is more accurate, after having precipitated the alumina by a potash-salt, to redissolve it in muriatic acid, and to precipitate it from this solution by means of ammonia, or better still, by carbonate of ammonia. When, therefore, the precipitated alumina has been sufficiently washed, the wet filter containing the alumina is put in a glass with muriatic acid to dissolve the alumina, the solution is filtered, the filter well washed, and the alumina is then precipitated again.*

\* As to the solution of magnesia it is made to boil for a long time. During the ebullition a great quantity of carbonic acid is evolved, on which account it should be performed in a large vessel, in order to afford room for the effervescence, which otherwise might occasion a loss. The best is to begin it in a flask,

and when the effervescence has ceased it is continued in a platinum capsula. The greatest part of the magnesia is thus precipitated in the state of carbonate of magnesia. As to the small portion which does not fall down, even by a prolonged ebullition, it is obtained either by rapidly evaporating the liquor to dryness, or by means of a solution of phosphate of soda, with addition of ammonia.

\* Bicarbonate of soda may be employed instead of bicarbonate of potash, to separate alumina from magnesia, but carbonate of ammonia cannot be used for the purpose, even when it contains an excess of carbonic acid.

#### SEPARATION OF ALUMINA FROM LIME.

The separation of alumina from lime presents some difficulty. The solution of these two earths is to be supersaturated with pure ammonia, by which alumina alone will be precipitated. But a precaution must be taken, which, if neglected, may often occasion most serious errors in quantitative analysis. It is well known that lime is not precipitated by ammonia, yet when a solution containing lime is supersaturated by ammonia, the liquor absorbs the carbonic acid of the air after a shorter or longer time, and crystals of carbonate of lime are deposited like grains of sand, some at the bottom, others on the sides of the glass, to which they adhere so strongly, that they cannot be completely detached from it by mechanical means: the more or less rapid formation of these crystals depends on the more or less considerable quantity of ammonia put in excess, or on the more or less dilute state of the solution. Consequently when alumina has to be separated from lime by means of ammonia, a large excess of this alkali should be avoided, and the alumina which will have precipitated should be thrown on a filter and collected as soon as possible in order to avoid its becoming mixed with carbonate of lime, and, moreover, the funnel, pending the filtering, should be kept covered with a glass plate, in order to avoid the contact of the air as much as possible.



\*The ammonia employed should be free from carbonate of ammonia,' which is always contained in that which has been kept a long time. In order to ascertain its purity it is put in a flask with a solution of chloride of calcium, or of barium, and if after some time the liquor has remained clear the ammonia contains no carbonate of ammonia; if, on the contrary, a slight turbidness is observed, it is owing to a formation of carbonate of lime or of baryta.

Oxalate of ammonia is then poured in the liquor filtered from the alumina, in order to precipitate the lime. The alumina is ignited and weighed, and water being poured upon it, concentrated muriatic acid is added; if this produces an effervescence, the operator concludes that it contains carbonate of lime.

\*In such a case the alumina should be completely redissolved in the acid, and be reprecipitated from that solution by ammonia, with the prescribed precautions, and the filtered liquor which contains a small quantity of lime should be mixed with that which contains already the larger quantity of the same base. If after having ignited the alumina, muriatic acid were immediately poured upon it a slight effervescence might often be produced, owing to a disengagement of air bubbles, expelled from the earth by the acid, which circumstance might lead the operator to think that this effervescence is due to a disengagement of carbonic acid, and consequently to the presence of carbonate of lime in the alumina. But if water be first poured upon the earth, this liquid expels the air, and if the further addition of muriatic acid now produces again a slight effervescence, there is no doubt but that it is due to carbonic acid, and consequently that the earth is mixed with carbonate of lime.

#### SEPARATION OF ALUMINA FROM MAGNESIA AND LIME.

When alumina has to be separated from lime and magnesia, muriate of ammonia is generally added to the solution, after

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<sup>1</sup> If the ammonia contains any carbonate of ammonia, carbonate of lime will be produced.—ED.

which the alumina is precipitated by means of pure ammonia perfectly free from carbonate of ammonia. If the solution is very acid the addition of muriate of ammonia is not necessary, because the ammonia employed for supersaturating it will produce enough ammoniacal salt. The precipitated alumina must be rapidly collected on a filter, in order to prevent any admixture of carbonate of lime. Oxalate of ammonia is then poured into the filtered liquor to precipitate the lime. The liquor filtered from the oxalate of lime thus produced, contains then *nearly* all the magnesia, for a small quantity of it has been carried down with the alumina. The latter earth is to be dissolved by a solution of pure potash as we said before, and the small quantity of magnesia thus separated is to be dissolved in muriatic acid. This solution is mixed with the liquor which has been filtered before from the precipitate of oxalate of lime, and which contains the greatest part of the magnesia. The magnesia is then precipitated by means of carbonate of potash or of soda in the manner which has been described above.

*A second method* for separating these two earths consists in pouring into their solution, one of bicarbonate of potash or of soda, for the purpose of precipitating alumina alone, and keeping the lime and the magnesia in solution. The liquor filtered from the alumina is evaporated to dryness. When the dry mass is afterwards treated by hot water, carbonate of lime and carbonate of magnesia are left behind, and they may then be separated from each other by one of the methods which have been described, when I have spoken of the determination of magnesia. In this case, however, the most advantageous method is that which consists in converting the two earths into sulphates, and in separating them from each other by solution of sulphate of lime.

We should remark, however, touching this mode of separating lime and magnesia, that it can be resorted to only when the quantity of lime is very small. The bicarbonate of potash employed, transforms the lime and the magnesia into bicarbonates of these

bases. Bicarbonate of magnesia is very soluble in water, whilst carbonate of lime is only very sparingly soluble, though more soluble in water containing free carbonic acid. Wherefore, when the quantity of lime is somewhat considerable, the solution should be diluted with a large quantity of water before adding bicarbonate of potash, yet, even in spite of this precaution, there is always reason to fear that the precipitated alumina may contain carbonate of lime.

\* If the solution of the earths is somewhat acid, there is no occasion to employ bicarbonate of alkali to precipitate the magnesia. Neutral carbonate of potash, or of soda, answers the same purpose, because the carbonic acid of the first portion added combines with the portion which is added afterwards, and which it converts into bicarbonate.

#### SEPARATION OF ALUMINA FROM STRONTIA.

For the purpose of separating alumina from strontia, pure ammonia is employed, just as for separating alumina from lime; the same precautions must be observed—the liquor must be filtered very rapidly out of the contact of the air, in order to prevent any admixture of carbonate of strontia, for the solutions of strontia, like those of lime, absorb, when mixed with ammonia, carbonic acid from the atmospheric air.

#### SEPARATION OF ALUMINA FROM BARYTA.

Alumina is separated from baryta by sulphuric acid, which precipitates the latter earth. To the liquid filtered from the precipitate of sulphate of baryta obtained, ammonia, or still better, carbonate of ammonia is added, which precipitates the alumina.

#### SEPARATION OF ALUMINA FROM THE ALKALIES.

Alumina is separated from the fixed alkalies by means of ammonia, or still better, by carbonate of ammonia, which precipitates the earth. The liquid filtered therefrom is evaporated to dryness, and the dry mass is to be ignited in a

counterpoised crucible. The ammoniacal salts produced by the union of the ammonia with the acid with which the alumina was combined, are thus volatilised, and the alkali remains combined with the acid with which it was united previous to the separation of the alumina. If the acid with which the alumina and the alkali were combined is sulphuric acid, it is necessary, in igniting the sulphate of alkali, to treat it by carbonate of ammonia, as we have said, (page 3).

SEPARATION OF ALUMINA FROM MAGNESIA, LIME, AND THE  
ALKALIES.

When alumina has to be separated from magnesia, lime, and a fixed alkali, which is very often the case, especially in the analysis of mineral substances, muriate of ammonia is first to be added to the solutions of these substances, after which, pure ammonia is poured in, by which alumina, mixed with a little magnesia, is precipitated. If the solution be very acid, there is no necessity for adding muriate of ammonia. The liquor is to be filtered rapidly to prevent the admixture of carbonate of lime with the precipitate. The lime is to be precipitated from the filtered liquor by oxalate of ammonia. The small portion of magnesia which has fallen down with the alumina, is separated by means of a solution of potash, and it is to be dissolved in an acid. This acid solution may be added to the liquor which has been filtered from the precipitate of oxalate of lime, (but as the magnesia might possibly retain a little alkali, it is better to precipitate it in the state of ammonio-magnesian phosphate). The liquor filtered from the lime is evaporated to dryness, the dry mass is ignited in order to expel the ammoniacal salts, and sulphuric acid being now cautiously added, the whole is heated and gently ignited. For separating the sulphate of magnesia from the sulphate of alkali, the process which we have indicated before, (page 40), may be followed.

\* If the solution contains muriatic acid, and no sulphuric or other acid, the separation may be effected by the method described, (page 43).

## CHAPTER IX.

## GLUCINIUM.

## DETERMINATION OF GLUCINIUM AND OF GLUCINA.

GLUCINA is completely precipitated from its solutions by pure ammonia. The precipitate has much resemblance with that of alumina. It is likewise very bulky, and contracts considerably in drying.

## SEPARATION OF GLUCINA FROM ALUMINA.

The usual method of separating glucina from alumina, is based upon the solubility of the first of these earths in carbonate of ammonia, and the separation may be effected in two ways.

According to the *first method*, a concentrated solution of carbonate of ammonia is to be added to the liquid, which contains the alumina and glucina; the flask is to be well closed, and allowed to stand for some time, stirring frequently. It is necessary to put a very large excess of carbonate of ammonia, because a small quantity of this reagent precipitates glucina, and it is only by using a very large proportion of carbonate of ammonia, that the precipitate produced at first is slowly redissolved. The operator will therefore observe that the voluminous precipitate, which is at first formed by the addition of the excess of carbonate of ammonia, gradually diminishes, because the precipitate is slowly dissolving. The alumina is then collected on a filter, washed, dried, and ignited, and its weight is then

determined. The liquor which is filtered from the alumina is evaporated to dryness in a porcelain, or better still, in a platinum capsula. As the carbonate of ammonia volatilises, the glucina is precipitated, and renders the liquor turbid. The dry mass is composed of glucina, and of a salt which the ammonia has produced with the acid with which the glucina and alumina were united. This dry mass is ignited, by which means the ammoniacal salt is dissipated, and glucina alone being left, it is weighed.

\* If, before the separation of the two earths, the liquor contained any fixed constituents, the carbonate of ammonia is cautiously supersaturated with muriatic acid, the solution is left standing until all the carbonic acid has escaped, and the glucina is precipitated by ammonia.

The *second method* of separating glucina from alumina is the following:—The two earths are precipitated together by means of pure ammonia. The voluminous precipitate is collected on a filter, and the filter is treated by muriatic acid and well washed. This solution and the still moist precipitate are put in a flask, and an excess of carbonate of ammonia being added, the whole is left to digest for a somewhat long time, by which means the glucina is gradually dissolved. The rest of the operation does not differ from the preceding one.

When glucina has to be separated from alumina, the first method is the best, but the second should be preferred in certain cases, when the two earths have to be precipitated together for the purpose of getting rid of certain substances with which they may be mixed.

\* Berthier proposed the following method of separating glucina from alumina:—The two earths are precipitated together from their solution by means of ammonia. The precipitate being washed, is to be tempered or diluted with water, and a current of sulphurous acid gas is passed through it until the whole is dissolved, after which the solution is boiled until all evolution of sulphurous acid has ceased. Basic sulphate of

alumina is precipitated under the form of a heavy powder, which is easily separated and washed. Glucina remains dissolved in the liquor from which it can be precipitated by ammonia. This method deserves to be preferred to that by carbonate of ammonia, because the latter salt, in dissolving the glucina, always takes up a small quantity of alumina<sup>1</sup>.

#### SEPARATION OF GLUCINA FROM MAGNESIA.

The first of the methods in use for separating alumina from magnesia, and of which I have given a description (page 52), may be resorted to for separating glucina from magnesia, for glucina, like alumina, is very soluble in solution of pure potash.

#### SEPARATION OF GLUCINA FROM LIME, STRONTIA, BARYTA, AND FROM THE ALKALIES.

Glucina may be separated from lime precisely in the same manner as alumina is separated from that substance, namely, by means of ammonia (page 51), and its separation from strontia, baryta, and the fixed alkalies, may be effected by the same means.

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<sup>1</sup> Messrs. Gmelin and Schaffgotsch have proposed the two following methods of separating glucina from alumina, both founded on the property which a solution of caustic potash possesses of dissolving glucina, and of abandoning it when the solution comes to be largely diluted with water, and boiled. The first of these processes consists in dissolving the two bases in a concentrated solution of potash, which is easily effected at a boiling temperature, and from which a portion of the glucina precipitates on cooling; the precipitation is completed by diluting largely with water, and boiling the whole. The second process consists in boiling the precipitates of the two earths in a weak solution of caustic potash, which dissolves the alumina only; the residuum is then to be well washed, and the glucina is separated therefrom by dissolving it in a concentrated solution of caustic potash. It is probable, says Berzelius, that the glucina which separates from a solution of potash, remains combined with some of that alkali, which renders it insoluble in the cold alkaline ley; but a prolonged washing removes the potash, and it again becomes soluble in the cold solution of potash.—Ed.

## CHAPTER X.

## THORINIUM.

## DETERMINATION OF THORINIUM AND THORINA.

\* **THORINA** is completely precipitated from its solutions by pure ammonia, and by a solution of pure potash. The precipitate obtained, especially by means of a solution of potash, is difficult to wash, like that of alumina.

\* Yet, according to Berzelius, thorina may be precipitated in a peculiar way, which permits its separation from other substances with which it may be mixed. If sulphate of potash is added in the solid form to the solution of this earth in an acid, no precipitate is at first produced, but gradually the liquor becomes turbid, and, by degrees, as the salt dissolves, a white crystalline powder is deposited at the bottom and on the sides of the glass vessel, which powder is a double sulphate of thorina and potash. When the solution of thorina is neutral, or very concentrated, the whole of the thorina precipitated in the state of double sulphate of thorina and potash cannot be obtained, because the sulphate of potash becomes very soon covered with a thin crust of double salt, which cannot be entirely removed by agitation, on which account the reaction is impeded. But if a solution of sulphate of potash, saturated at a boiling heat, is poured, whilst still hot, in the solution of thorina, until it ceases to become turbid, the thorina is, after cooling, found entirely precipitated, even though the solution contained an excess of acid. Yet it is well, if the solution of thorina is very acid, to



pour ammonia into it, almost to saturation, before adding the sulphate of potash. The double sulphate of thorina and potash must be washed with a saturated and cold solution of sulphate of potash, in which this salt is perfectly insoluble. After which, boiling water is poured upon it whilst on the filter, by which it is dissolved without residuum. The thorina may then be precipitated from the solution by one of pure potash<sup>1</sup>.

#### SEPARATION OF THORINA FROM ALUMINA AND GLUCINA.

\* This separation is effected by means of a solution of pure potash, into which the two latter earths are soluble. The solution which contains the earths is precipitated by an excess of solution of potash, into which the precipitate of thorina obtained should be boiled. The precipitate is then separated by filtering, after which the alumina and glucina may be precipitated from the filtered alkaline liquor by the methods which have been indicated, (page 56).

#### SEPARATION OF THORINA FROM MAGNESIA.

\* Berzelius has effected this separation by adding ammonia to the acid solution of the two earths in muriatic acid, by which the thorina is precipitated, whilst the magnesia is held in solution by the muriate of ammonia produced.

#### SEPARATION OF THORINA FROM LIME.

\* This separation is easily effected by means of ammonia when these two earths are in solution. The precipitated thorina must be filtered rapidly, because, without this precaution, it might, whilst in contact with the air, become mixed with carbonate of lime.

#### \* SEPARATION OF THORINA FROM THE ALKALIES.

This separation is likewise effected by means of ammonia.

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<sup>1</sup> The precipitated earth after being well washed, dried, and ignited, may then be weighed. It is important to ignite it, because it is the only means of obtaining it pure, in which state it is white; but the smallest trace of oxyde of manganese is sufficient to give it a yellowish tinge.—Ed.

## CHAPTER XI.

## YTTRIUM.

## DETERMINATION OF YTTRIUM AND YTTRIA.

YTTRIA may be precipitated from its solutions by pure alkalies. It is not advantageous, according to Berzelius, to use pure ammonia for the purpose, because hydrate of yttria is slightly soluble in the ammoniacal salt produced. It is better to employ pure potash; but in many cases in which this reagent cannot be employed, ammonia is resorted to; yet from solution of sulphate and nitrate of yttria, potash precipitates basic salts.<sup>1</sup> Wherefore, when the operator is obliged to employ a solution of potash to precipitate yttria from a liquor containing sulphuric acid, the solution must be left for some time in contact with the precipitate. The basic sulphate precipitated must then be ignited which volatilises part of the sulphuric acid, and the residuum is afterwards dissolved in dilute nitric acid, or in muriatic acid, and the liquor must then be precipitated again by solution of potash.

\* A good method for separating yttria from a great number of solutions, consists in precipitating it in the state of oxalate. Oxalate of yttria is completely insoluble in water, and even in

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<sup>1</sup> Ammonia poured in a solution of chloride of yttrium precipitates yttria in the state of hydrate, but from solutions of sulphate or of nitrate of yttria, ammonia precipitates the yttria, not in the state of hydrate, but in that of a basic salt, and therefore the use of solution of potash is recommended in such cases instead of ammonia; yet, as *potash* precipitates basic salts also from such solutions, the operator must proceed as directed in the text.—ED.

very dilute nitric acid and in muriatic acid. The solution from which yttria has to be separated, is, therefore, rendered neutral or very feebly acid by means of muriatic acid, and then a solution of oxalic acid is poured into it. By igniting the oxalate of yttria produced, it is very easily converted into pure yttria, free from carbonic acid.

**\* SEPARATION OF YTTRIA FROM ALUMINA AND GLUCINA.**

Yttria is separated from alumina and glucina by heating the solution of these two earths with a solution of potash, and leaving the two liquors to digest together for a long time, whereby the alumina and glucina are dissolved.

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**SEPARATION OF GLUCINA FROM YTTRIA.**

Note by M. E. Peligot in the French edition :—

According to Berthier, these two oxydes may be separated by adding sulphite of ammonia to their solution and boiling the whole ; the yttria is thus precipitated in the state of basic sulphite entirely insoluble in water, but soluble in sulphurous acid ; the glucina remains in the solution, and it is afterwards precipitated by ammonia.

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**SEPARATION OF YTTRIA FROM MAGNESIA.**

Yttria may be separated from magnesia by ammonia, after having added muriate of ammonia to the solution.<sup>1</sup>

**SEPARATION OF YTTRIA FROM LIME, STRONTIA, BARYTA, AND  
THE ALKALIES.**

Yttria may be separated from these bases by the same means which are employed for the separation of alumina from these earths. In such cases ammonia must be employed for the precipitation of yttria.

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<sup>1</sup> Of course for the purpose of keeping the magnesia in solution.—Ed.

## CHAPTER XII.

## CERIUM.

## DETERMINATION OF CERIUM AND OF ITS OXYDES.

THE oxydes of cerium can be precipitated from their solutions by pure ammonia, but a solution of pure potash is preferable, because, according to Berzelius, the precipitate produced by ammonia consists chiefly of subsalts of cerium instead of pure oxydes. The precipitate is dried, ignited, and weighed. After ignition it is a peroxyde, into which even the protoxyde, if it was in that state previous to being ignited, is converted. When the substance under examination contains protoxyde of cerium only, its quantity is to be calculated from that of the peroxyde obtained.

## SEPARATION OF THE OXYDES OF CERIUM FROM YTTRIA.

According to Berzelius, for the purpose of separating the oxydes of cerium from yttria with which they are often mixed, a process somewhat similar to that for separating thorina from several substances is used. To the solution, either acid or neutral, containing yttria and the oxydes of cerium, or only one of them, a crust of crystallised sulphate of potash is added. The best way of employing this reagent is, to place the crystalline crust of the salt into the liquid, so that it should be a little above the level of the liquid, in order that all its parts may become saturated with sulphate of potash. The oxydes of yttrium and of yttria possess

the property of producing double salts by combining with potash and sulphuric acid ; but among these double salts, that which is produced by yttria is soluble, whilst those which result from the combination of the oxydes of cerium are insoluble in a saturated solution of sulphate of potash. The precipitate produced by the oxydes of cerium is pulverulent, and has a white colour when it contains protoxyde of cerium, and a lemon-yellow colour when it contains peroxyde of cerium. It is allowed to subside, and after twenty-four hours it is collected on a filter, when the solution is saturated with sulphate of potash, and it is washed with a saturated solution of the latter salt, after which it is dissolved in boiling water and precipitated therefrom by a solution of pure potash, a pretty large excess of which must be used, and into which it must be left to digest, with the help of heat ; if this precaution be neglected, there is a risk of the precipitate containing basic salts. After having washed this precipitate, it is ignited, by which it acquires a cinnamon-brown colour, and is completely converted into peroxyde of cerium, even if it consisted of protoxyde of cerium before ignition. The liquor from which the oxydes of cerium have been separated, contains then a double sulphate of yttria and potash. The yttria is then precipitated by means of solution of potash, and this precipitate is treated as we have said, (page 63).

SEPARATION OF THE OXYDES OF CERIUM FROM THE EARTHS  
AND THE ALKALIES.

The oxydes of cerium are separated from glucina, alumina, magnesia, lime, strontia, baryta, and the fixed alkalies, in the same manner as for separating yttria from these substances.

## CHAPTER XIII.

## ZIRCONIUM.

## DETERMINATION OF ZIRCONIUM AND ZIRCONIA.

ZIRCONIA is precipitated from its solutions by pure ammonia, and also by a solution of pure potash ; yet it very often happens that ammonia precipitates the zirconia, not in the state of pure zirconia, but in the state of basic salts. After having washed the precipitate which is voluminous, it is moderately ignited, an operation during which the zirconia becomes incandescent, and afterwards it is weighed.

According to Berzelius, zirconia is also precipitated when a solution of sulphate of potash is mixed with one of a salt of zirconia. If sulphate of potash in crystals has been added in sufficient quantity to saturate the liquor with it, the greater part of the zirconia is precipitated ; and the separation of this earth may be completed by exactly neutralising the acid contained in the solution with potash. A basic sulphate of zirconia containing potash is thus produced ; and as this salt is partially soluble in pure water, it should be washed with water to which a little ammonia has been added ; it is then boiled with a solution of pure potash, and pure hydrate of zirconia remains. Thus can zirconia be separated from certain substances.

## SEPARATION OF ZIRCONIA FROM THE EARTHS AND ALKALIES.

Zirconia, like the oxydes of cerium, yttria, and especially glucina, is soluble in the carbonates of alkalies ; and, according

to Berzelius, it dissolves with the greatest facility, especially in bicarbonate of potash, or of soda, though the zirconia previously precipitated dissolves therein excessively slowly. But when a solution of zirconia is poured drop by drop in one of bicarbonate of soda or of potash, the solution is very rapidly effected: zirconia is precipitated from the solution by boiling, adding muriate of ammonia and boiling again. In effect, a portion of the zirconia is dissolved by the excess of carbonic acid, and it is that portion which the boiling precipitates. Another portion is dissolved in the simple carbonate of alkali, and that portion is precipitated by the ammonia of the muriate of ammonia which is decomposed.

Zirconia may be thus separated from alumina; and it can, by the same process, be separated from magnesia, lime, strontia, baryta, and the fixed alkalies. But accurate means of separating it from the oxydes of cerium, yttria, and glucina, are still wanting. The best method as yet known, according to Berzelius, is the following:—The boiling solution is mixed with sulphate of potash, by which most of the zirconia is precipitated in the state of a basic salt; a little ammonia is added to the acid solution, but not in sufficient quantity to supersaturate the free acid, otherwise the oxydes of cerium, yttria, and glucina would be precipitated. The basic sulphate of zirconia is washed with pure water, in which, however, it is slightly soluble; it is then treated by a solution of pure potash, as we have said before. As to the liquor filtered from the salt of zirconia, the other bases may be precipitated therefrom in the manner previously described.

## CHAPTER XIV.

## MANGANESE.

## DETERMINATION OF PROTOXYDE OF MANGANESE.

PROTOXYDE of manganese [*oxyde manganeux*] may be precipitated by several of the reagents employed for precipitating magnesia, which it much resembles as regards its chemical properties. The best of these re-agents is *carbonate of potash*, and especially *carbonate of soda*, because the latter may easily be obtained free from silicic acid. The precipitation of the protoxyde of manganese by the carbonates of alkalies, requires that many precautions should be observed, which I have detailed at length in speaking of the determination of magnesia.

\* It is advisable to warm the liquor gently after the addition of the carbonate of alkali, and it is not necessary that the precipitation should take place at a boiling heat; neither is it necessary after having filtered the liquor from the protocarbonate of manganese precipitated to evaporate it to dryness by a strong heat.

Protocarbonate of manganese is insoluble in water<sup>1</sup>, consequently it can be washed better than carbonate of magnesia. It is then dried and ignited in a platinum crucible, and weighed. Ignition deprives it of its carbonic acid, and converts it into brown manganoso-manganic oxyde, to effect which, however, a

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<sup>1</sup> Protocarbonate of manganese is soluble in water, which contains free carbonic acid, in which respect it resembles the carbonate of the alkaline earths, and is, like them, very often met with in mineral waters.—Ed.



rather elevated temperature is required, though inferior to a white heat. From the weight of this manganoso-manganic oxyde that of the protoxyde of manganese is calculated when the substance contained it in that state<sup>1</sup>.

When the liquor, from which protoxyde of manganese has to be precipitated, contains considerable quantities of muriate or other salts of ammonia, it must be boiled with an excess of carbonate of alkali, until the odour of ammonia is entirely dissipated<sup>2</sup>.

Protoxyde of manganese is, like magnesia, precipitated also by solution of pure potash<sup>3</sup>. The precipitate which is a hydrate of protoxyde has at first a white colour, but whilst washing it upon the filter, its colour changes very soon, owing to an absorption of oxygen, and becomes brownish black, beginning from the surface<sup>4</sup>. It may likewise be converted into manganoso-manganic oxyde by a strong ignition. It is, however, in few cases only that pure potash is resorted to for the precipitation of protoxyde of manganese; carbonate of alkali being generally preferred.

Protoxyde of manganese may be determined in the state of sulphate, when it exists alone in a liquor from which no other substance has to be quantitatively separated, and which contains no other fixed constituents; but this method of determination does not yield results so accurate as with magnesia. When protosulphate of magnesia is ignited in contact with the air, it loses a small portion of its acid, owing to which, after ignition, a very small portion of the salt can no longer be dissolved by

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<sup>1</sup> The heat should be continued so long as the weight of the crucible does not remain constant.—Ed.

<sup>2</sup> This is absolutely necessary, because recently precipitated protocarbonate of manganese being readily dissolved by muriate or other salts of ammonia, it is impossible to precipitate the whole of the manganese in presence of these salts, and therefore they should be completely decomposed, exactly as has been described for the precipitation of magnesia by carbonate of potash, page 35.—Ed.

<sup>3</sup> Hydrate of protoxyde of manganese is soluble in solution of muriate of ammonia; see vol. i. page 62.—Ed.

<sup>4</sup> If this precipitate be dried in the air, it turns brown throughout, and it is then a hydrate of sesquioxys of manganese.—Ed.

water. This quantity, however, is very trifling when the sulphate of manganese has not to be too strongly ignited, and this method may be resorted to in a great many cases for the purpose of determining expeditiously the quantity of protoxyde of manganese. The process is the same as that which we have described previously in the article Magnesium (page 33). It is advisable, when this method is employed, to avoid a very large excess of sulphuric acid, because it is difficult to expel it without at the same time losing a portion of the residuum.

DETERMINATION OF DEUTOXYDE (*sesquioxysde*) AND PEROXYDE (*deutoxyde*) OF MANGANESE.

If manganese is contained in the state of *sesquioxysde* of manganese in the liquor, which is frequently the case, it may be precipitated by ammonia. The precipitate of *sesquioxysde* is converted into manganoso-manganic oxyde by a strong ignition; but as this transformation often requires so strong a heat that it cannot always be obtained by a spirit-lamp with circular wick, and that even by a moderate heat the operator cannot be perfectly sure that the oxyde will not have lost a portion of its oxygen, it is often advisable to begin by converting the *sesquioxysde* or *sesquichloride* into protoxyde or protochloride of manganese. The best method of effecting this, consists in adding muriatic acid to the solution, and to warm it for a long time; the *sesquichloride* is thereby converted into protochloride of manganese, under disengagement of chlorine. The operator must not, instead of muriatic acid, use sugar, gum, or organic substances of the kind in the solution, as has been proposed by several chemists. True, that the conversion of *sesquichloride* of manganese into protochloride can be accomplished in this manner, but the presence of non-volatile organic substances may, in a great number of cases, hinder the precipitation of substances by alkalis. Alcohol, however, is the best substance to be used, in case the operator

should employ such a method for transforming sesquioxide into protoxyde of manganese.

When the operator has to examine sesquioxide of manganese either in the native state or in combination with water, or peroxyde of manganese and substances which contain it, the best is, if those substances contain no other fixed constituents besides manganese, to expose them to a red heat until it be converted into manganoso-manganic oxyde.<sup>1</sup> The loss of weight is due to the expulsion of oxygen, provided the combination contains no other volatile substance, such as water, for example. I shall explain farther on (article Hydrogen) by what method the weight of the water can be determined.

\* There are several methods of estimating the commercial value or quantity of peroxyde of manganese, and that of foreign substances contained in a sample of this substance. The manganese of commerce, which it is intended to analyse, must first be reduced into fine powder, which is then to be treated by dilute nitric acid, in order to dissolve all the earthy carbonates which it contains. If the analysis is made for a technical purpose, the weight of these carbonates should be determined. The best way is to take a certain weight of manganese, and to digest it for a long time with dilute nitric acid, until it has dissolved all it can; the mass is then dried until the weight remains constant, and it is weighed. The difference between the two weights expresses the quantity of the earthy carbonates which have been dissolved.

\* The simplest and best manner of analysing the manganese is the following. A certain quantity of the purified and well-dried manganese is introduced in a small counterpoised retort, to which a counterpoised tube, containing chloride of calcium, is adapted. After calcining it, the augmentation of the weight of the chloride of calcium indicates the quantity of water which has volatilised, and which proceeds from the hydrated sesquioxide, a portion of which is always contained in the peroxyde :

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<sup>1</sup> Under the influence of a red heat, and with the contact of the air, all the oxydes of manganese are converted into manganoso-manganic oxyde.—Ed.

the diminution of the weight of the retort indicates how much water and oxygen have escaped. Yet it is not possible, by merely calcining in the retort, to convert the peroxyde of manganese completely into manganoso-manganic oxyde; wherefore the contents of the retort must be emptied in a small platinum crucible and therein ignited, until, after repeatedly weighing it, the weight remains constant. The mass becomes thus completely converted into manganoso-manganic oxyde. If the ignition is carried on with a spirit-lamp with circular wick, small quantities only must be operated upon, and the mass must be kept red hot for a long time, in order to obtain a complete conversion. When the quantity of the mass is considerable, an ordinary fire is used. 100 of oxygen disengaged, represent 818.85 of pure peroxyde. Whence it may be seen that great precision is required in this experiment, since a small quantity of oxygen corresponds to a great quantity of peroxyde. 100 parts of water evaporated, correspond to 981.76 of hydrate of sesquioxido.<sup>1</sup>

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<sup>1</sup> M. Ebelmen's method of analysis is as follows :—The oxyde of manganese under examination, is treated by muriatic acid, and the chlorine disengaged is received in a solution of pure sulphurous acid, part of which acid is converted into sulphuric acid. When the reaction is completed, solution of chloride of barium, and a little muriatic acid, are poured in the liquor; the muriatic acid being employed for dissolving the sulphite of baryta, which is produced simultaneously with the sulphate, and which, being but sparingly soluble, would remain mixed with it; the liquor is then boiled, for the purpose of expelling the excess of sulphurous acid, filtered, and the precipitate of sulphate of baryta is dried, from the weight of which the quantity of the peroxyde of manganese contained in the sample is calculated: 100 of sulphate of baryta corresponds to 37.5 of peroxyde of manganese.—Ed.

Another method is that of M. Thomson, which is founded on the quantity of carbonic acid, which is produced by the reaction of sulphuric acid upon a given weight of the oxyde, with a solution of oxalic acid. One equivalent of oxalic acid produces 2 equivalents of carbonic acid, weighing almost as much as 1 equivalent of peroxyde of manganese. The *modus operandi* is as follows :—600 grammes of water 50 grammes of oxalic acid, 50 grammes of the manganese under examination, and lastly, and as quickly as possible, 150 or 200 grammes of concentrated sulphuric acid are introduced into a counterpoised flask; carbonic acid is immediately disengaged, at first rapidly, and then slowly: twenty-four hours afterwards the apparatus is weighed, and the loss of weight indicates the weight of the peroxyde of manganese. Instead of oxalic acid, Messrs. Fresenius and Will employ oxalate of potash, and the proportions are, one part in weight of a given quantity of the manganese, and two and a half of neutral oxalate of potash, and one-third of the capacity of the

Manganoso-manganic oxyde is a degree of oxydisement of manganese, which, according to the experiments of Arfvedson, does not change by exposure to a red heat; protoxyde and protocarbonate of manganese are easily transformed into this state, when strongly ignited in a platinum crucible above a spirit-lamp with circular wick, provided the access of the air be not completely prevented. Sesquioxide and peroxyde of manganese require exposure to a stronger heat and for a longer time for their conversion into manganoso-manganic oxyde.

If foreign bodies exist still in the substance under analysis, it should be dissolved in muriatic acid with the help of heat, and the foreign fixed constituents with which the protoxyde of manganese may be mixed, must be separated from the solution.

SEPARATION OF PROTOXYDE OF MANGANESE FROM ZIRCONIA,  
THE OXYDES OF CERIUM, YTTRIA, AND THORINA.

The same process which is employed for separating zirconia, the oxydes of cerium, yttria, and thorina, from magnesia, may be adopted for separating protoxyde of manganese from these substances. Protoxyde of manganese is not precipitated by ammonia when the solution contains a very large quantity of muriate of ammonia. The other substances, on the contrary, are precipitated by this alkali. There is a precaution which it is important to observe in performing this operation; it is to filter as rapidly as possible, and out of the contact of the air; because the protoxyde of manganese contained in the ammoniacal solution, very soon absorbs oxygen and then separates in the state of sesquioxide. Yet it is difficult to separate protoxyde of manganese completely in this manner.

\* *Another method* consists in igniting the mixture of the

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flask is filled with water: two or three parts of sulphuric acid are now added; the rest of the operation is the same as mentioned before. These methods, however, presuppose, of course, the absence of carbonates in the sample, otherwise the sample should first be washed with some dilute nitric acid, and then with pure water, and dried. Other methods will be indicated farther on.—Ed.

earths and of the protoxyde of manganese, and treating the ignited mass with weak nitric acid free from nitrous acid; the acid dissolves the earths and leaves the manganoso-manganic oxyde undissolved. The separation of protoxyde of manganese from the oxydes of cerium and from thorina is better effected by sulphate of potash than by ammonia; these substances being precipitated by the sulphate of potash in the manner described, (pages 61-65). When these substances have been thus separated, the protoxyde of manganese may then be precipitated also.

\* Some of the earths which have just been mentioned might be separated from protoxyde of manganese by carbonate of baryta, in the manner which may be employed for separating them from peroxyde of iron, and which will be described farther on.

#### SEPARATION OF PROTOXYDE OF MANGANESE FROM ALUMINA AND GLUCINA.

Ammonia and muriate of ammonia may also be employed for separating protoxyde of manganese from alumina and glucina. But then, and even when the liquor contains much muriate of ammonia, pure ammonia always precipitates a little protoxyde of manganese with the alumina and glucina. This is observable because the precipitated earths very soon turn brownish in contact with the air, the small quantity of protoxyde of manganese precipitated along with the earths becoming thus converted into sesquioxyde of manganese. Wherefore the precipitated glucina and alumina should be redissolved in a solution of pure potash, which has no action upon sesquioxyde of manganese. In a word, the operation should be conducted as for the separation of magnesia from alumina by means of ammonia, as we have said before, (page 54).

Alumina and glucina can also be separated immediately from protoxyde of manganese by means of potash. The solution of these substances is slightly boiled with an excess of pure potash.

Yet, if the liquor contains much ammoniacal salt, it is better and less expensive to decompose it by carbonate of potash with the help of heat.

Bicarbonate of potash, on the contrary, cannot be used for separating protoxyde of manganese from alumina, because protoxyde of manganese is dissolved in extremely small quantity by that salt.

#### SEPARATION OF PROTOXYDE OF MANGANESE FROM MAGNESIA.

To the solution of these two substances, enough muriate of ammonia is added to prevent the ammonia, which has to be poured in it afterwards, from producing a precipitate. If the solution is acid, there is no occasion for adding muriate of ammonia, because the ammonia employed to saturate it, produces a sufficient quantity of ammoniacal salt. Hydrosulphuret of ammonia is then added in sufficient quantity to precipitate the whole of the protoxyde of manganese in the state of sulphuret of manganese. It is not even necessary that the hydrosulphuret of ammonia should not contain any free ammonia. The protoxyde of manganese is precipitated in the state of sulphuret of manganese, with the characteristic flesh colour, or, if in pretty large quantity, the precipitate is redder. This sulphuret contains no sulphuret of magnesium, if enough hydrosulphuret of ammonia has been added. When the precipitate has perfectly settled, the liquor is filtered. If the operator were to attempt to filter it before the complete settling of the precipitate, it would pass through the paper too slowly. The sulphuret of manganese is then washed, not with pure water, but with water to which a little hydrosulphuret of ammonia has been added, in the proportion of about three or four drops per ounce of water. After washing, the sulphuret of manganese on the filter changes colour very soon, it absorbs oxygen, and becomes at the surface first brown, and then black. The rapidity with which sulphuret of manganese becomes oxydised, renders it absolutely necessary that the precipitation and washing should succeed

each other immediately, and it is for the same reason that the quantity of protoxyde of manganese cannot be calculated from the weight of this sulphuret. Wherefore, it must be cautiously introduced with the moist filter in a glass, and muriatic acid is poured upon it, which causes a disengagement of sulphuretted hydrogen. The whole is heated very gently until the liquor smells no longer of sulphuretted hydrogen. It is then to be filtered, and the protoxyde of manganese is precipitated therefrom, by carbonate of potash, or of soda. The protoxyde of manganese may also be converted into sulphate of protoxyde of manganese, as we have already said, (page 70).

The liquor filtered from the sulphuret of manganese contains the whole of the magnesia. It is first to be rendered slightly acid, by adding muriatic acid thereto, in order to destroy the excess of hydrosulphuret of ammonia employed, and it is left in digestion for a long time, until it smells no longer of sulphuretted hydrogen. It is then to be filtered from the very finely divided sulphur which this will have separated, and the magnesia may then be quantitatively determined in the filtered liquor, by means of carbonate of potash, or of soda, or what is better still, by converting it into sulphate of magnesia.

Often, also, magnesia and protoxyde of manganese are precipitated together by carbonate of potash, then dissolved by muriatic acid, and then separated from each other in the manner which has been described.

Stromeyer has indicated *another method* of separating protoxyde of manganese from magnesia. A current of chlorine gas is to be passed through the liquor which holds both these substances in solution, and which is generally effected by muriatic acid. This current of chlorine gas in the cold produces perchloride of manganese. A solution of bicarbonate of potash poured in the liquor, precipitates the sesquioxys of manganese, but not the magnesia. If the liquor be now evaporated to dryness, by a strong heat, the magnesia may be obtained. Stromeyer prescribed, in order to precipitate the magnesia, to



use a solution of phosphate of soda, to which ammonia has been added.

\* Instead of chlorine gas, the aqueous solution of chlorine may be employed when feeble quantities only of protoxyde of manganese have to be separated. If, on the contrary, the protoxyde of manganese is more abundant, bromine may be employed with advantage.

#### SEPARATION OF PROTOXYDE OF MANGANESE FROM LIME.

Several methods may be resorted to for the purpose of separating protoxyde of manganese from lime. If only a small quantity of protoxyde of manganese has to be separated from a very large quantity of lime, the solution is to be first diluted with water, if not already sufficiently dilute, and enough of a solution of muriate of ammonia is added to prevent the ammonia, which is subsequently added to slight supersaturation, from producing a precipitate. If the solution is acid, there is no necessity for adding muriate of ammonia; the lime may then be precipitated by means of oxalate of ammonia, and the whole is heated in order that the oxalate of lime produced may be rapidly filtered,<sup>1</sup> for when the filtering is delayed, the salt is mixed with a small quantity of sesquioxide of manganese, owing to the protoxyde of manganese in the liquor having absorbed oxygen, and thus become insoluble. The protoxyde of manganese is then precipitated from the liquor filtered from the oxalate of lime, or else it may be converted into protosulphate of manganese.

The method which I have just described, however, is not applicable when the quantity of protoxyde of manganese to be separated from lime is very large. In such cases, it is in effect not only much more difficult to avoid an admixture of protoxyde of manganese with the oxalate of lime, but a small quantity of oxalate of protoxyde of manganese may actually be precipitated with the latter salt, especially if the liquor be not very dilute.

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<sup>1</sup> See the note, page 33, where I have given the description of my filtering apparatus.—Ed.

It is better, therefore, in such cases, to resort to another process. Muriate of ammonia is added to the liquor in sufficient quantity to prevent the ammonia, which is added subsequently, from producing a precipitate. This addition of muriate of ammonia is not necessary when the liquor is acid, because by supersaturating it with ammonia, enough of an ammoniacal salt is produced. The protoxyde of manganese is then precipitated in the state of sulphuret of manganese, by means of hydrosulphuret of ammonia; the sulphuret is allowed to settle a little, and the liquor is to be filtered very rapidly, taking care to cover the funnel and the beaker with a glass plate, in order, as much as possible, to avoid the contact of the air, for fear that the sulphuret should become contaminated with carbonate of lime. The best is, before adding the hydrosulphuret of ammonia, to put the liquor in a flask which can be closed, in order that the sulphuret may settle well without fear of the contact of the air. After having washed the sulphuret with water, to which a little hydrosulphuret of ammonia has been added, it is treated by muriatic acid in the manner which has been previously described. As to the liquor which has been filtered from the sulphuret of manganese, muriatic acid is added to it in sufficient quantity to render it acid, in order to decompose the excess of hydrosulphuret of ammonia, and then it is gently heated until all smell of sulphuretted hydrogen has vanished. During this operation, there is always a separation of a small portion of sulphur which should be first filtered from the liquor, from which, after supersaturation with ammonia, the lime is precipitated by oxalate of ammonia.

This method is very preferable to the first, because, according to Turner, oxalate of lime is a little soluble in a liquor which contains much of a protosalt of manganese.

Gaseous bromine, or chlorine, may also be employed with advantage to separate protoxyde of manganese from lime. The manganese having thus been converted, in the muriatic acid solution of the two bases, into sesquichloride, or bromide of manganese, the liquor is introduced into a flask, susceptible of

being well corked, and a slight excess of ammonia being poured therein, the oxyde of manganese is precipitated, the flask is corked up to prevent the contact of the air, and the oxyde is allowed to settle completely. The clear, supernatant liquor is decanted, the oxyde washed very rapidly, to prevent the admixture of carbonate of lime from the contact of the air, and the lime is precipitated from the filtered liquor by means of oxalate of ammonia.

If the oxalate of lime, which has been thus separated, contains a little oxalate of manganese, it must first be ignited, treated by very dilute nitric acid, which dissolves the carbonate of lime, and leaves behind the manganoso-manganic oxyde produced.

SEPARATION OF PROTOXYDE OF MANGANESE FROM ALUMINA,  
MAGNESIA, AND LIME.

When alumina, magnesia, and lime, have to be separated from protoxyde of manganese, the process varies according to the quantity of the latter substance.

If the quantity be small, muriate of ammonia is added to the liquor, which precaution, however, is useless when it contains free acid, the alumina is then precipitated by ammonia, which always precipitates at the same time traces of magnesia and of protoxyde of manganese. During the filtering the alumina is sheltered as much as possible from the contact of the atmospheric air, in order to prevent the formation of carbonate of lime. The lime is then precipitated from the filtered liquor by means of oxalate of ammonia. In order to separate the traces of protoxyde of manganese and of magnesia which have been precipitated along with the alumina, it is to be treated by potash in the manner which has been indicated, (page 76). The small quantities of protoxyde of manganese and of magnesia are dissolved in muriatic acid, and mixed with the liquor which has been filtered from the oxalate of lime. The protoxyde of manganese is separated from the magnesia in the manner which has been described before.

When, on the contrary, the quantity of protoxyde of man-

ganeses is pretty considerable, the process is as follows :—After having precipitated the alumina, together with traces of magnesia and of protoxyde of manganese, by means of ammonia, the liquor is filtered, and sulphuret of manganese is precipitated by means of hydrosulphuret of ammonia. The liquor filtered from the sulphuret of manganese is rendered acid by muriatic acid, and heated until all smell of sulphuretted hydrogen is dissipated ; it is then filtered, supersaturated with ammonia, and the lime is precipitated by oxalate of ammonia. The sulphuret of manganese is dissolved in muriatic acid. The operator may mix together the solution of sulphuret of manganese, the muriatic acid solution of the traces of protoxyde of manganese and of magnesia which have fallen down with the alumina, and which have been separated therefrom by potash, and the liquor filtered from the oxalate of lime, after which the magnesia may be separated from the protoxyde of manganese. It is better, however, to precipitate the protoxyde of manganese from the solution of sulphuret of manganese, and then to precipitate the magnesia alone from the liquor filtered from the oxalate of lime, and to analyse also separately, and determine quantitatively, the traces of magnesia and of protoxyde of manganese which have been precipitated along with the alumina.

#### SEPARATION OF PROTOXYDE OF MANGANESE FROM STRONTIA.

Protoxyde of manganese may be separated from strontia in the following manner. To the solution of the two bases, enough muriate of ammonia is added to prevent the formation of a precipitate by the subsequent addition of ammonia. If the liquor is acid, there is no need to add muriate of ammonia, it is sufficient to pour ammonia into it. Protoxyde of manganese may then be precipitated in the state of sulphuret of manganese, but in filtering it the contact of the air must be avoided, in order to prevent the formation of carbonate of strontia. The liquor filtered from the sulphuret of manganese must be rendered acid, and again filtered to separate the liberated sulphur, and

the strontia may then be separated. This method is preferable to that which consists in precipitating strontia by sulphuric acid, because sulphate of strontia is not absolutely insoluble in water.<sup>1</sup>

#### SEPARATION OF PROTOXYDE OF MANGANESE FROM BARYTA.

Protoxyde of manganese is separated from baryta by sulphuric acid, in the same manner as for separating magnesia from baryta. According to the experiments of Turner, baryta exists in almost all the ores of manganese.

#### SEPARATION OF PROTOXYDE OF MANGANESE FROM THE ALKALIES.

The separation of protoxyde of manganese from the fixed alkalies is not difficult. After having added ammonia to the liquor, so as to render it alkaline, protoxyde of manganese is precipitated in the state of sulphuret of manganese. The liquor filtered from it is rendered acid, it is then heated, filtered, and the quantities of the alkalies in the filtered liquor may be determined in the manner which has been described before.

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<sup>1</sup> Sulphate of strontia, according to Dr. Fresenius, is soluble in 6895 parts of cold water, at 140 centigrade, and in 9638 of boiling water.—Ed.

## CHAPTER XV.

## IRON.

DETERMINATION OF IRON, PROTOXYDE OF IRON, PEROXYDE OF IRON, AND COMPOUNDS OF PROTOXYDE AND OF PEROXYDE OF IRON (*Oxyde Ferroso-ferrique*).

WHETHER iron exists in the substance to be analysed in the state of metal, of protoxyde, or of peroxyde of iron, or in the state of ferroso-ferric oxyde, it is never determined except in the state of PEROXYDE OF IRON.<sup>1</sup> If the compound contains metallic iron, protoxyde of iron, or ferroso-ferric oxyde, it must be dissolved in nitric acid, or in aqua regia. The solution contains then the iron in the state of peroxyde of iron. When a liquor contains protoxyde of iron, or ferroso-ferric oxyde, nitric acid is added, and heat applied, by which means it is converted into peroxyde of iron. If the solution is very dilute, the complete peroxydisation by nitric acid seldom takes place without heating the liquor almost to boiling; or, if nitric acid is not employed, without passing a current of chlorine through it, or adding a sufficient quantity of bromine; all which means, however, are not so good as that by nitric acid. When the quantity of protoxyde of iron is pretty considerable, the liquor, after addition

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<sup>1</sup> According to Liebig (*Annal. der Chemie und Pharm.* Bd. xli., heft. 3), iron may be determined in the dry way, in a direct manner, by means of cyanide of potassium. The ore is first to be reduced to powder, and a mixture of cyanide of potassium and of carbonate of potash being added, the whole is exposed to a strong red heat in a porcelain crucible. The alumina and silica remain with the scories, and the reduced iron may be separated by washing with cold water, and then weighed.—ED.

of nitric acid, and the application of a gentle heat, becomes black, and almost opaque, without depositing any precipitate; but it soon becomes clear again, which is a sign that a sufficient quantity of nitric acid has been added, and that the whole of the protoxyde is converted into peroxyde. The black colour of the liquor is produced by nitric oxyde, resulting from the decomposition of the nitric acid, and which is dissolved by the solution of the protoxyde of iron as yet undecomposed.

When the liquor contains peroxyde of iron only, ammonia is the reagent employed to precipitate it, which it does completely. The precipitate is reddish brown, and very voluminous. It already shrinks a little, like that of alumina, whilst being washed on the filter; but on drying, it reduces in bulk in an extraordinary degree; and after ignition it forms a hard vitreous mass of a brownish black colour. If the liquor be heated after precipitation, the precipitate becomes more dense and darker. After drying, it is ignited, during which operation it sometimes decrepitates, on which account the heat should be cautiously applied at the beginning. Ignition upon a spirit-lamp with circular wick does not deprive it of any oxygen, and the filter may even be burnt with it without reducing a single particle, provided the draft of air be suitably kept up.<sup>1</sup> It sometimes happens, but not always, that whilst igniting the peroxyde a vivid disengagement of light is observed.

From the weight of the peroxyde of iron, the quantity of the iron, of the protoxyde of iron, or of the ferroso-ferric oxyde in the combination is calculated.

The peroxyde of iron may also be completely precipitated by potash, but it is then difficult to wash, and it always retains a little potash, which may in the analysis apparently produce a slight excess of peroxyde of iron. When, therefore, potash has been employed to precipitate peroxyde of iron, the latter should be redissolved in muriatic acid, and reprecipitated by ammonia.

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<sup>1</sup> Should there be, however, any fear of a portion of the peroxyde having been reduced by the charcoal of the filter, a few drops of nitric acid may be poured on the ignited mass, which will at once redissolve it, and by a second ignition the whole is obtained in the state of peroxyde.—ED.

Peroxyde of iron is completely precipitated also by carbonate of potash, and by carbonate of ammonia,<sup>1</sup> when the solution of the peroxyde of iron is neutral. If the liquor is acid, the bicarbonate of alkali which is produced retains in solution a very small trace of peroxyde of iron, which cannot be completely precipitated except by boiling the liquor for some time.

In a very great number of cases peroxyde of iron is precipitated in the state of SULPHURET OF IRON, to separate it from other substances. When the liquor is acid, it is to be neutralised by ammonia, a slight excess of which may be employed which produces, it is true, a precipitate of peroxyde of iron, but which is not objectionable. Hydrosulphuret of ammonia is next added, until all the peroxyde of iron is converted into sulphuret of iron, which deposits very slowly under the form of a voluminous black precipitate. When the supernatant liquor has only a yellowish tinge due to the excess of hydrosulphuret of ammonia employed, the sulphuret of iron must be rapidly collected on a filter, and washed with water to which hydrosulphuret of ammonia has been added.

The liquor often remains coloured green after the sulphuret of iron has settled ; \* this takes place more especially when it contains much organic substance, such as, for example, tartaric acid.

This colour is due to the presence of extremely fine particles of sulphuret of iron, which remain suspended in the liquid, and which very often require a very considerable length of time to settle. If the solution be filtered in that state, it passes green through the filter, but in such cases it suffices to warm the green liquor gently, and for a long time, upon a sand bath, out of the contact of the air, before filtering it; the sulphuret of iron is thus deposited completely, and the supernatant liquor has only a yellowish tinge.

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<sup>1</sup> If carbonate of ammonia is added in larger proportion, however, the hydrate of peroxyde of iron may be entirely redissolved ; but Berzelius observes, that whatever be the excess of carbonate of ammonia employed, the hydrate of peroxyde of iron may be completely precipitated from such a solution, by diluting with a sufficient quantity of water. The hydrated oxydes of iron are slightly soluble in solution of potash.—Ed.



The sulphuret of iron on the filter absorbs the oxygen of the air very rapidly, and in a short time its surface soon acquires a light reddish brown colour, which gradually pervades the whole mass. The rapidity with which it becomes oxydised is cause that the quantity of the oxyde of iron cannot be calculated from its weight, and it must, therefore, be converted into peroxyde of iron. It should, therefore, be treated about in the same manner as the precipitate of sulphuret of manganese. Whilst still moist it is to be put in a glass, with the filter, and muriatic acid is poured upon it, by which it is immediately dissolved under a disengagement of sulphuretted hydrogen; the whole is then warmed gently until all smell of sulphuretted hydrogen has disappeared. The liquor is then filtered, the filter is well washed, nitric acid is added to the filtrate, and heat is applied. The iron which existed in the state of protoxyde in the solution, is converted by the nitric acid into peroxyde of iron, which may then be precipitated by ammonia.

The sulphuret of iron, with the filter, must not be treated immediately by aqua regia, for the purpose of at once converting the iron, which it contains, into peroxyde of iron. In effect, the action of aqua regia upon some sorts of paper produces organic substances, which might oppose the precipitation of the peroxyde of iron by ammonia.

When the iron has to be precipitated in the state of sulphuret of iron, whatever may be the degree oxydisation of the iron in the liquor is of no consequence. Protoxyde of iron is precipitated by hydrosulphuret of ammonia absolutely in the same state as peroxyde of iron.

If the sulphuret of iron obtained be strongly ignited, the access of the air, instead of being altogether excluded, being, on the contrary, admitted as much as possible, this may, of itself, be sufficient to convert it completely into peroxyde of iron. Yet, to obtain this result, a heat is required stronger than can be produced with an argand spirit-lamp. The necessary heat, however, may easily be obtained by putting the sulphuret of iron, with the filter, in a small counterpoised platinum capsula

or crucible, and exposing it in a muffle to the heat of a cupelling furnace. But, if the sulphuret of iron be only in small quantity, it is sufficient, in order to convert it into peroxyde of iron, to expose it to a red heat in contact with the air in a platinum crucible.

SEPARATION OF PEROXYDE OF IRON FROM PROTOXYDE OF  
MANGANESE.

The following process is employed to separate peroxyde of iron from protoxyde of manganese :—

If the two oxydes are dissolved in an acid, for example, in muriatic acid, muriate of ammonia is first added to the solution, especially when the protoxyde of manganese is very abundant in proportion to the peroxyde of iron, and then it is to be very exactly saturated with ammonia. If the solution be very acid, there is no occasion for adding muriate of ammonia, because the saturation of the acid by ammonia produces a sufficient quantity of ammoniacal salt. The saturation with ammonia is difficultly executed, especially when there is a large proportion of protoxyde of manganese. When the solution is pretty near the point of saturation, the alkali should be poured in with great care. The best is then to make use of very dilute ammonia, which may be poured, drop by drop, in the liquor, until it has become of a very dark red colour, or until a little peroxyde of iron begins to precipitate, and is not redissolved by stirring.<sup>1</sup> Yet, the liquor which floats above this precipitate must be dark red, and retain in solution the greatest part of the peroxyde of iron. If the whole of the latter substance has been precipitated by the addition of too large a quantity of ammonia, dilute muriatic acid is again to be added, drop by drop, in order to redissolve the greatest part of the peroxyde of iron.<sup>2</sup>

This being done, a solution of neutral succinate of ammonia is now added to the liquor, which produces an abundant precipitate

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<sup>1</sup> Nor even by gently warming the liquor.—Ed.

<sup>2</sup> The operator may know that he has added too much ammonia, and that the whole of the peroxyde of iron has been precipitated, because in that case the liquor above the precipitate, instead of being dark red, is colourless.—Ed.

of a cinnamon colour, which is persuccinate of iron, and which is much more bulky than the precipitate of peroxyde of iron produced by ammonia. Yet, the colour of the precipitate is not of a pure cinnamon colour when the peroxyde of iron has already been partly precipitated by ammonia. All these precautions must be attended to, in order not to precipitate any trace of manganese. When, before adding succinate of ammonia, a certain portion of peroxyde of iron has been precipitated, but yet the greatest part of this oxyde remains still in solution, and communicates a red colour to the liquor, the operator may rest assured that no trace of protoxyde of manganese has been precipitated with the peroxyde of iron. If, before adding succinate of ammonia, the liquor had not been properly saturated by ammonia, it might happen subsequently that traces of persuccinate of iron would remain in solution.

When peroxyde of iron has to be precipitated in the state of persuccinate of iron from a neutral solution of a persalt of iron, it is clear that the neutral succinate of ammonia may be immediately poured in. Yet it is better to add a small quantity of ammonia to the solution of the persalt of iron before adding the succinate of ammonia. After complete cooling, the persuccinate of iron is collected on a filter, and washed with cold water, for the use of hot water often decomposes it, and dissolves an acid persuccinate of iron.<sup>1</sup> It sometimes happens also that the cold water dissolves a little of the persuccinate of iron during the washing, but this takes place only when the water from which it has been precipitated was acid. It is good to warm the whole gently, but it should be allowed to cool completely before filtering it.<sup>2</sup>

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<sup>1</sup> According to Dr. Fresenius, cold water must be used instead of hot water ; not because persuccinate of iron is decomposed by hot water, but because, if an excess of succinate of ammonia has been employed, one equivalent of succinic acid is set free, which in the cold and dilute state has not much action upon the precipitated persuccinate of iron, but which in the hot state is capable of redissolving a portion of it.—Ed.

<sup>2</sup> It is good to warm the whole gently, because this removes the chance of resolution in washing. It is evident, also, that, in order to be sure that the whole of the iron has been precipitated as persuccinate of iron, the operator must add neutral succinate of ammonia, so long as a precipitate is thereby determined.—Ed.

Crystallised *succinate of soda* may also be employed to effect this precipitation, because it can always be obtained in the neutral state. In general, however, the neutral succinate of ammonia is employed, and in a great number of cases it is the only one which may be had recourse to. But the crystallised succinate of ammonia should not be used, because it is an acid salt. The salt may be obtained in the neutral state by saturating dilute ammonia with succinic acid.

After washing and drying the succinate of iron it is to be ignited. Whilst igniting it in a platinum crucible, it is necessary to place a cold body across the crucible, in order to promote a current of air, and thus prevent the carbon of the succinic acid from reducing a little peroxyde of iron. When there is only a small quantity of persuccinate of iron, the reduction of the least trace of peroxyde of iron by the heat can be easily prevented, but if the quantity of the salt be larger, this becomes more difficult. Yet after having washed the persuccinate of iron, the greatest part of the succinic acid can be removed by pouring dilute ammonia upon it whilst on the filter; the alkali takes up a certain portion of the acid, by which the bulk of the precipitate is diminished, and its colour rendered darker.<sup>1</sup>

The protoxyde of manganese may be separated from the liquor filtered from the persuccinate of iron by precipitating it in the state of carbonate of manganese by means of carbonate of potash, or else it may be transformed into sulphuret of manganese. In the latter case it is clear that the peroxyde of iron must have been precipitated by succinate of ammonia, and not by succinate of soda.

This method of separating peroxyde of iron from protoxyde of manganese is attended with no difficulty when the quantity of the peroxyde of iron is very considerable, but if this oxyde be less abundant it is not easy to neutralise the liquor in such a way that the greatest part of the peroxyde of iron remains still in solution, and only a small portion be precipitated, for one single drop of

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<sup>1</sup> Dr. Fresenius recommends that the dilute ammonia employed for washing should be warm, because it then removes the acid more completely.—Ed.

dilute ammonia is often sufficient to precipitate the whole of it if the quantity be very small.<sup>1</sup> The difficulties are still augmented if the quantity of protoxyde of manganese is at the same time very considerable, for it may then happen that a portion of the protoxyde of manganese may be converted into sesquioxycide by absorption of the oxygen of the air, and be precipitated with the peroxyde of iron. When, therefore, the quantity of peroxyde of iron to be separated from a large quantity of protoxyde of manganese is small, it is best to adopt the following plan, namely: muriate of ammonia is to be added to the liquor, and the peroxyde of iron is precipitated therefrom by caustic ammonia. If the liquor is very acid there is no occasion to pour muriate of ammonia. Care must be taken not to use an excess of ammonia, and the precipitated peroxyde of iron must be filtered as rapidly as possible, in order to prevent the oxydisation of the protoxyde of manganese. The peroxyde of iron precipitated in this way is mixed with some protoxyde of manganese, it is therefore redissolved in muriatic acid, from which solution it is reprecipitated by succinate of ammonia in the state of persuccinate of iron, an operation which is easily effected, because the solution then contains much peroxyde of iron and little protoxyde of manganese.

According to Hisinger, the benzoates may very well be substituted for the succinates, peroxyde of iron being likewise completely precipitated by them. In such a case the same precautions must be attended to as have been recommended when the succinates are employed. Formerly, when benzoic acid was less

<sup>1</sup> If the quantity of peroxyde of iron is very small, an exceedingly minute quantity of dilute ammonia may be added, to the extent of half a drop, or a quarter of a drop, or even less, by means of a pipette, which I generally make with the neck of a broken retort. It is, therefore, a conical tube, drawn to a fine point, as represented in the figure. The dilute ammonia is sucked up or poured in the tube, and by pressing the tip of the finger on the upper extremity, the contents are pushed out in very minute drops. The point may be so fine, that each drop will not weigh more than the 40th part of a grain.—Ed.



expensive than succinic acid, there was some advantage in using it instead of succinic acid, now, however, it is quite the reverse, succinic acid being cheaper than benzoic acid. Moreover, the precipitate of benzoate of iron is still more bulky than that of the succinate, and as benzoic acid contains much more carbon than succinic acid, the reduction of a little oxyde of iron during the ignition of the benzoate of iron is still more to be apprehended. Yet the benzoate may, as well as the succinate, be deprived of the greatest portion of its acid by ammonia.

*\* Another method* of separating peroxyde of iron from protoxyde of manganese was recommended by Fuchs. It consists in the employment of CARBONATE OF LIME, which precipitates peroxyde of iron, but which does not precipitate a trace of protoxyde of manganese. The two oxydes are first dissolved in muriatic acid. If the manganese was united with peroxyde of iron in the state of sesquioxido of manganese, it is thereby converted into protochloride of manganese with the help of heat. If the iron exists in the state of protoxyde of iron, the solution is effected in aqua regia, in order to convert it into peroxyde of iron. A great excess of acid should be avoided. The substance being dissolved, the liquor is to be warmed, and pulverised carbonate of lime added by degrees. It is better to employ the carbonate of lime, which the operator will have precipitated by carbonate of ammonia, from a solution of pure chloride of calcium.

*\* Carbonate of lime* is further added, stirring the liquor at the same time, until bubbles [of carbonic acid] have ceased to be evolved, and so that there be an excess of carbonate of lime. It is absolutely necessary to avoid carefully the application of heat.<sup>1</sup> The peroxyde of iron falls down with the excess of carbonate of lime in the form of a light brown powder. It is allowed to settle well, it is collected on a filter and washed with hot water. This done, and whilst it is on the filter, muriatic acid is poured

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<sup>1</sup> If this direction be not attended to, there will be danger of some manganese falling along with the peroxyde of iron.—ED.

on it, the solution thus obtained is filtered, and the peroxyde of iron may be precipitated therefrom by ammonia. The precipitate must be carefully sheltered from the contact of the air, in order that it should not be contaminated by carbonate of lime.

\* The peroxyde of iron being thus separated from the carbonate of lime, the filtered liquor is to be introduced in a flask susceptible of being well corked, and the protoxyde of manganese may then be precipitated free from the lime contained in the liquid, by means of hydrosulphuret of ammonia (page 78).

\* Yet this method cannot be employed and is not preferable to that by means of succinate of ammonia, except in rare cases.<sup>1</sup> Carbonate of baryta may be used instead of carbonate of lime, as Fuchs was also the first to suggest, and this reagent is much more advantageous, because it is much easier to eliminate baryta than lime by means of sulphuric acid. Carbonate of baryta is used exactly in the same manner as carbonate of lime, an excess of it is likewise employed, and it is filtered after a lapse of time, which must not be too long, the application of heat being also carefully avoided. The peroxyde of iron separates with the excess of carbonate of baryta, and the protoxyde of manganese remains in solution. After filtering, the precipitate and the filter are treated by muriatic acid, and when the precipitate has completely dissolved, the baryta is to be precipitated by dilute sulphuric acid; the liquor is then heated, and then after separating the sulphate of baryta, the peroxyde of iron may be precipitated by ammonia. If the experiment has been performed with due precaution not a trace of protoxyde of manganese will have precipitated. Dilute sulphuric acid is also poured in the liquor, for the purpose of precipitating the baryta which is held in solution, and after the separation of sulphate of baryta, the protoxyde of manganese may be separated.

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<sup>1</sup> This method can be employed only when the metallic oxides present are combined with acids which do not form insoluble compounds with lime, or with baryta; and, therefore, the muriatic acid solution must not contain sulphuric acid, arsenic acid, phosphoric acid, nor boracic acid, since the salts of lime and of baryta, with these acids, are insoluble, or only sparingly soluble.—En.

In all these operations, it is necessary that the solution which contains the peroxyde of iron and the protoxyde of manganese, should not contain any sulphuric acid nor phosphoric acid, nor arsenic acid.

\* There are cases when this mode of separation by carbonate of baryta is preferable to that by succinate of ammonia; but the latter generally takes less time, and on that account is more often resorted to.

\* Herschel, who had already for a long time used this method, or one of a similar nature, for the purpose of separating peroxyde of iron from several other oxydes, does not employ either carbonate of lime or of baryta. His method is grounded upon this: that the peroxyde of iron of the neutral or slightly basic persalts of that metal, is precipitated from the solutions of these salts by boiling, whilst the other oxydes, for example, protoxyde of manganese, remain in solution. The solution is saturated in the cold by one of carbonate of ammonia, either exactly or in such a manner, that a slight precipitate of peroxyde of iron begins to appear. The whole is then boiled, the peroxyde of iron falls down, whilst the protoxyde of manganese remains dissolved.<sup>1</sup>

#### SEPARATION OF PROTOXYDE OF IRON FROM PROTOXYDE OF MANGANESE.

The first thing to be done is to convert the protoxyde of iron into peroxyde of iron, and the operation is then carried on as we have just said. The conversion is effected, with the help of heat, by aqua regia, which does not cause the protoxyde of manganese to pass to a higher degree of oxydisation.

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<sup>1</sup> M. Scheerer has proposed another process, which consists in dissolving the two oxydes in sulphuric acid, and saturating the solution with caustic potash, until the reaction is neither acid nor alkaline. The peroxyde of iron is at first partially precipitated, but the whole of it is completely thrown down when, water being added, the solution is made to boil. It is then to be filtered, and the basic salt obtained being washed, the quantity of peroxyde of iron which it contains may be easily determined. This process, it may be seen, is a modification of Herschel's. When



## SEPARATION OF PEROXYDE OF IRON FROM ZIRCONIA.

Peroxyde of iron is separated from zirconia in the following manner:—

To the diluted solution of these two substances, one of tartaric acid is added. This acid possesses the property, when mixed with the solutions of a great number of metallic oxydes and of earths, to prevent their being precipitated by alkalies; this is precisely the case with peroxyde of iron and zirconia. When, therefore, a sufficient quantity of tartaric acid is added to the solution of these two substances, the ammonia which is subsequently added does not produce any precipitate. Hydrosulphuret of ammonia is then poured in until it ceases to produce a black precipitate. The peroxyde of iron is thereby precipitated in the state of sulphuret of iron, whilst the zirconia does not experience any change. When the precipitate has completely settled, and the supernatant liquor has only a yellowish colour, it is to be filtered without delay; if, on the contrary, the liquor remains greenish, the whole must be digested at a very gentle heat, and out of the contact of the air, until the liquor has become of a yellowish colour. The sulphuret of iron must be rapidly washed with water, to which a little hydrosulphuret of ammonia has been added, and it is then converted into peroxyde of iron in the manner which has been indicated before (page 86).

The liquor filtered from the sulphuret of iron is evaporated to dryness, and the dry residuum is ignited in a counterpoised platinum crucible with the contact of the air until it has become white. This result, however, is somewhat difficult to obtain when the dry mass is pretty considerable, because the carbon of the tartaric acid requires a long time to burn completely; yet its combustion can be effected more easily by putting the

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this mode of operating is adopted, sulphuric acid must be employed, and nitric acid and muriatic acid avoided, because the basic nitrate of iron, and basic chloride of iron, are slightly soluble.—ED.

dry mass in a small counterpoised platinum capsula, and introducing it in the mouffle of a small assay furnace. The zirconia obtained is then weighed. If the tartaric acid contains any fixed foreign substances, such as *lime*, for example, they are found at the end, mixed with the zirconia.

\* Berthier proposed *another method* for separating zirconia from the oxydes of iron, in solutions. The muriatic acid solution of these substances are to be first saturated by a current of sulphuretted hydrogen, an excess of ammonia is then added, which precipitates both the zirconia and the sulphuret of iron produced. The precipitate is allowed to settle out of the contact of the air; the supernatant liquor, which contains hydrosulphuret of ammonia, is decanted as much as possible, and to the precipitate an aqueous solution of sulphurous acid is immediately added in sufficient quantity to make it smell distinctly of it. The sulphuret of iron is thereby converted into hyposulphite of iron, which dissolves, whilst the zirconia remains with a white colour. The latter is collected on a filter, washed, and weighed. As to the liquor which was filtered from it, it is to be oxydised by nitric acid, and the iron which it contains is estimated as peroxyde of iron.

\* If the excess of sulphurous acid had dissolved traces of zirconia, they might be completely separated by boiling the liquor.

#### SEPARATION OF PEROXYDE OF IRON FROM THE OXYDES OF CERIUM.

Peroxyde of iron is separated from the oxydes of cerium by means of sulphate of potash, in the manner explained (page 65), for separating these oxydes from yttria.

#### SEPARATION OF PEROXYDE OF IRON FROM YTTRIA.

Peroxyde of iron may be separated from yttria by the same process which is employed for separating it from zirconia, yet the following process is generally adopted:—The solution of the

two substances is to be first saturated with ammonia, and the peroxyde of iron is then precipitated by succinate of ammonia; the yttria is next precipitated from the liquor filtered from the persuccinate of iron by adding a further quantity of ammonia thereto.

\* It is necessary to remark, however, that the solution should be diluted; that after the precipitation of the peroxyde of iron by succinate of ammonia, the whole should be heated; and that the precipitate of peroxyde of iron must be collected on a filter immediately after cooling; for succinate of yttria, although sparingly soluble, does not precipitate immediately, but only after some time in concentrated solutions; but when once precipitated, it is difficultly soluble in cold water, though hot water dissolves it more readily.<sup>1</sup>

#### SEPARATION OF PEROXYDE OF IRON FROM THORINA.

This separation is effected by means of sulphate of potash as has been indicated (page 61).

#### SEPARATION OF PEROXYDE OF IRON FROM GLUCINA AND ALUMINA.

This separation is effected by means of potash. The solution is reduced to a rather small bulk by evaporation; it is then to be mixed in a porcelain capsula, or, better still, in one of platinum, with a solution of pure potash, and it is then gently boiled. All is at first precipitated thereby; but when a sufficient quantity of potash has been employed, the alumina and glucina are redissolved. As the two earths are gradually dissolving, the undissolved portion becomes of a darker brown

<sup>1</sup> Scheerer proposed oxalate of potash as a means of separating peroxyde of iron from yttria. The solution is first to be rendered neutral, after which the addition of oxalate of potash produces, after some time, a precipitate which is a double oxalate of yttria and potash: the iron remains in solution. The precipitate should be allowed to settle in a warm place, for about twenty-four hours before filtering. The dried and ignited precipitate must then be redissolved in muriatic acid, and the resolution must be diluted with a large quantity of water. Ammonia being now added, precipitates the yttria, which may then be filtered, washed, ignited, and weighed.—Ed.

colour, and ultimately consists only of peroxyde of iron. The liquor is then to be filtered, and the peroxyde of iron must be washed; the liquor filtered therefrom must now be super-saturated by muriatic acid and the alumina is precipitated by carbonate of ammonia, the glucina by pure ammonia. If the two earths exist simultaneously in the solution, they may be separated by the process which has been indicated (page 58). When great accuracy is required, the peroxyde of iron should be redissolved by means of muriatic acid and reprecipitated by ammonia.

The drawback of this method is, that an inexperienced chemist cannot know whether he has added a suitable quantity of potash to the liquor containing the peroxyde of iron, the alumina and glucina, for the deep brown colour of the undissolved peroxyde of iron may induce him into error. It is only after having separated it from the glucina and alumina dissolved in the potash that he may know whether he have employed a sufficient quantity of potash; this is ascertained by letting a drop of muriatic acid fall in the liquor. If a small cloud is thereby formed, due to a liberation of alumina or of glucina, and if the small cloud disappear by agitation, there is an excess of potash. This proof, however, cannot be much depended upon when the quantity of alumina or of glucina, combined with the peroxyde of iron, is very small<sup>1</sup>.

#### SEPARATION OF PEROXYDE OF IRON FROM MAGNESIA.

Magnesia is separated from peroxyde of iron by the same process which is employed for separating it from protoxyde of manganese. To the solution of magnesia and of peroxyde of

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<sup>1</sup> Another process was proposed by M. Berthier, for separating solutions of alumina, glucina, and peroxyde of iron, and other solutions of oxydes, grounded upon the property which the hydrates, or carbonates of certain bases possess of being dissolved by sulphurous acid, and of being precipitated, or not, from such a solution, by boiling. In the present case, by adding solution of sulphurous acid to that containing the above substances, and boiling until the smell of sulphurous acid has disappeared, the liquor becomes discoloured, because the peroxyde of iron is reduced to that of protoxyde, and the alumina falls down, whilst the glucina remains in solution

iron, muriate of ammonia is first added and then an excess of ammonia. If the solution is acid, the addition of muriate of ammonia is needless. Ammonia always precipitates a small quantity of magnesia with the peroxyde of iron, even when much muriate of ammonia has been employed. The precipitate is dissolved in muriatic acid; after which the liquor is exactly saturated with ammonia, and the peroxyde of iron is precipitated by neutral succinate of alkali, with the precautions which have been detailed before (page 88). The liquor separated from the persuccinate of iron, and which contains a small quantity of magnesia, is mixed with that which was filtered from the precipitate of peroxyde of iron produced by ammonia, and which contains the greatest part of the magnesia. The magnesia is afterwards precipitated from the liquor which then contains the whole of this earth.<sup>1</sup>

\* Of course, if the quantity of peroxyde of iron is not too small in comparison with that of magnesia, the solution of the two bases is to be immediately saturated with ammonia, and the peroxyde of iron is precipitated in the state of persuccinate, by means of a succinate of alkali. The method which has just been indicated, is applicable only when the quantity of the magnesia is very large, and that of the peroxyde of iron very small.

According to Fuchs, magnesia may, like protoxyde of manganese, be separated from peroxyde of iron by means of carbonate of lime, or of baryta (page 91).

#### SEPARATION OF PEROXYDE OF IRON FROM LIME AND STRONTIA.

Peroxyde of iron is precipitated from lime and strontia by means of ammonia, which does not precipitate these two earths. The peroxyde of iron is separated by filtering, and the two

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together with the iron, and may be subsequently separated by the methods which have been described. This process, however, does not give accurate results, M. Bottinger having proved that the precipitates which sulphurous acid produces are not pure; added to which, they become oxydised during the washing, and soluble sulphates are formed, which of course are washed away.—Ed.

<sup>1</sup> When there is a sufficient quantity of muriate of ammonia in the liquor, the

earths may then be separated from the filtered liquor, as has been described. It is only necessary here to filter and to wash the precipitated peroxyde of iron rapidly, and to avoid, as much as possible, the contact of the air during the filtering, for, if this precaution be not taken, it might be contaminated by carbonate of lime, or of strontia.

\* It is right, however, after having ignited and weighed the peroxyde of iron obtained to ascertain that it contains no earthy carbonates in the manner which has been indicated in the chapter on alumina (page 54).

#### SEPARATION OF PEROXYDE OF IRON FROM BARYTA.

Peroxyde of iron is separated from baryta by means of sulphuric acid, and it may be precipitated from the liquor filtered from the sulphate of baryta produced, by means of ammonia.

#### SEPARATION OF PEROXYDE OF IRON FROM THE ALKALIES.

Ammonia is the reagent employed to separate peroxyde of iron from the fixed alkalies. The alkalies are contained in the filtered liquor, and they are obtained by evaporating it to dryness, and igniting the dry residuum.

#### SEPARATION OF PEROXYDE OF IRON FROM PROTOXYDE OF MANGANESE, ALUMINA, MAGNESIA, LIME, AND THE ALKALIES.

When peroxyde of iron has to be separated from several of the substances of which we have spoken in the preceding paragraphs, the method to be adopted may be inferred from the precepts which have been related. If, for example, peroxyde of iron is to be separated from protoxyde of manganese, alumina, magnesia, lime, and a fixed alkali, proceed as follows:—To the solution add a sufficient quantity of muriate of ammonia, which,

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peroxyde of iron precipitated by ammonia contains only a trace of magnesia, and therefore, except when great accuracy is required, the re-solution in muriatic acid, and re-precipitation by succinate of ammonia, may be dispensed with.—Ed.

however, need not be done if the solution be very acid, and then supersaturate it with pure ammonia; the precipitate which is thereby produced must be very rapidly collected on a filter, avoiding the contact of the air as much as possible. The lime is precipitated from the filtered liquor by oxalate of ammonia. Ammonia will have precipitated the peroxyde of iron and alumina, as well as small quantities of magnesia, and of protoxyde of manganese. The precipitate is dissolved in muriatic acid, an excess of which must be avoided, and boiled with a solution of potash. The alumina is thereby dissolved, which may subsequently be precipitated from the filtered liquor in the manner described before (page 57). The potash has left the peroxyde of iron undissolved, and mixed with a small proportion of magnesia, and of protoxyde of manganese<sup>1</sup>. This residuum is dissolved in muriatic acid, the solution is diluted with water, saturated with ammonia, and the peroxyde of iron is precipitated by succinate of ammonia. The liquor filtered from the persuccinate of iron obtained, is mixed with that which was filtered from the oxalate of lime. Hydrosulphuret of ammonia is poured into it, in order to precipitate the protoxyde of manganese in the state of sulphuret of manganese; the liquor is filtered, it is rendered acid by pouring some muriatic acid into it, in order to destroy the excess of hydrosulphuret of ammonia employed, heat is applied, it is filtered again, evaporated to dryness, the dry residuum is ignited, after which, it is treated by sulphuric acid, and the liquor is evaporated to dryness; the residuum is ignited with carbonate of ammonia, in order to convert the bisulphate of alkali into neutral sulphate,<sup>2</sup> and it is then weighed.

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<sup>1</sup> In boiling the precipitate with solution of potash, for the purpose of separating alumina from peroxyde of iron, the former, which is thereby dissolved, always retains a small portion of iron; wherefore M. Kopp proposed (*Journal für Pract. Chem.*, vol. xxxix.) to precipitate the two substances by hydrosulphuret of ammonia, as was recommended by Messrs. Malagutti and Durocher, wash it with water to which some hydrosulphuret of ammonia has been added, and separate the two oxydes from each other by means of solution of potash to which a few drops of hydrosulphuret are added. The alumina obtained in this manner is perfectly white.—ED.

<sup>2</sup> See p. 3, and note 1.

The weight of the sulphate of magnesia, and of the sulphate of alkali, is then determined, after which, these two substances are separated from each other in the manner which has been mentioned before (page 42).

\* It is better to precipitate separately the small quantities of magnesia, and of protoxyde of manganese, the solution of which has been separated from the persuccinate of iron by filtering, and not to mix it with the solution which was separated from the oxalate of lime, when the latter contains still some alkali. The small quantities of magnesia, and of protoxyde of manganese, which have been separated from the alumina conjointly with the peroxyde of iron, by potash, may contain a little alumina.

The course of this analysis must be modified when the quantity of the protoxyde of manganese is very considerable—that is to say : before precipitating the lime by oxalic acid, the greatest part of the protoxyde of manganese must be precipitated by hydrosulphuret of ammonia, as we have said, (page 79).

**DETERMINATION OF THE QUANTITIES OF PROTOXYDE AND OF PEROXYDE OF IRON WHEN THEY EXIST SIMULTANEOUSLY IN A COMPOUND.**

The determination of these two oxydes is always attended with many difficulties, which are much more increased still when these two oxydes are accompanied by a great number of other constituents, and, when the compound is not soluble in acids, it is often altogether impossible to overcome these difficulties.

If the compounds to be analysed contain protoxyde and peroxyde of iron only, and are soluble in acids, as, for example, the native magnetic iron ore (load stone), and the various kinds of scales of iron produced by exposing iron to a red heat in contact with the air, a certain quantity must be dissolved in muriatic acid. Nitric acid is added to the solution, and the whole is heated, in order to convert the protoxyde of iron into peroxyde of iron ; the liquor is then diluted with water and



ammonia being added, the peroxyde of iron is thereby precipitated, after which, it is washed, dried, ignited, and weighed. From the weight of the peroxyde of iron thus obtained, the quantity of oxygen absorbed by the substance to convert the protoxyde of iron into peroxyde of iron is known, and by the tables printed at the end of this work, the quantity of the protoxyde of iron is estimated. When this has been determined, the quantity of the peroxyde of iron contained in the substance, is deduced from the difference of weight between the quantity of the substance operated upon, and that of the protoxyde of iron found by calculation.

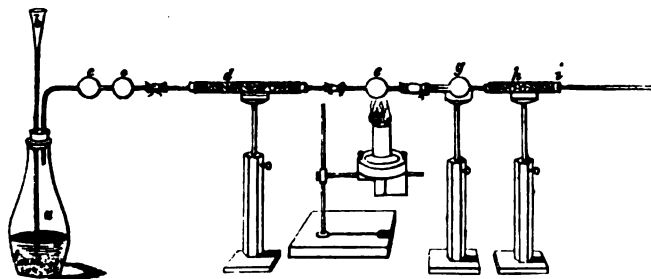
It may be easily conceived that the greatest precision is required in such an analysis. In the combinations of peroxyde and of protoxyde of iron, the quantity of the first is ordinarily very considerable compared to that of the second. The excess of weight obtained, when the substance is completely converted into peroxyde of iron, is therefore very feeble, and an error however trifling committed in determining it, produces a very considerable error in the estimation of the protoxyde of iron.

If the substance to be analysed contains small quantities of constituents which are insoluble in muriatic acid, for example, silicic acid, as is almost always the case both with the native magnetic iron ore and the different species of scales of iron above mentioned, the solution is filtered to separate it from the insoluble portions, the weight of which is ascertained and subsequently deducted from the substance under examination.

The quantity of oxygen which exists in a combination composed solely of proto- and of peroxyde of iron, may be estimated in another way. The two oxydes are reduced into the state of metallic iron, by passing a current of dry hydrogen gas over them whilst exposed to heat. The quantity of water produced by the oxygen of the oxydes of iron, and by the hydrogen gas employed, must be determined.

The experiment is performed in the following manner:—Hydrogen gas is disengaged in a flask *a*, closed with a cork

perforated with two holes. Through one of these holes a funnel *b*, is passed, which funnel has a long neck. Through the other hole a disengagement tube bent at right angle is passed, on which two bulbs *c c*, have been blown. Pieces of zinc are



put in the flask *a*, which is next to be filled about one-third full, taking care that the tube of the funnel *b*, plunges below the surface of the liquid. Sulphuric acid is gradually poured through this funnel into the flask, by which means a current of hydrogen gas is slowly disengaged, and escapes through the disengagement tube. A great portion of the aqueous vapour mixed with the hydrogen gas, is condensed in the bulbs *c c*; the gas, however, contains as yet a certain quantity of moisture, of which it is completely deprived by making it pass through a glass tube *d* filled with fused chloride of calcium, connected by a tube of caoutchouc to the disengagement tube; the other end of the chloride of calcium tube is also connected by means of another tube of caoutchouc to another glass tube provided with a bulb *e*. This bulb *e*, should be made of pretty strong glass, in order that it should not fuse by the heat to which it is subjected, wherefore, instead of blowing it in the middle of the tube, it is better to take a small bulb of strong glass, and to solder a small glass tube at each side of it. The small glass tube the farthest from the tube containing chloride of calcium, is to be drawn to a point.

The empty bulb *e*, with the two small glass tubes soldered to it, must first be exactly weighed, and the quantity of the substance to be analysed is then introduced, taking care that

the whole quantity penetrates into it; the two small tubes on each side are scrupulously cleaned with the feather of a quill, and the bulb is then weighed again. The increase of weight indicates the quantity of the substance to be analysed contained in the bulb.

In most cases it is best to employ the substance in the pulverised state, because it is then more easily decomposed by hydrogen; and also, but more especially, in order to avoid a loss which would take place when the substance decrepitates on the first application of heat, as is most often the case with the minerals found in nature.

To the bulb *e*, another bulb *g*, of a similar kind is connected by means of an Indian-rubber tube, in such a way that the small glass tube, drawn to a point, penetrates into the latter bulb *g*, to which another small tube *h*, containing fused chloride of calcium is adapted, taking care that one of the two tubes on each side of the bulb *g*, traverses the cork of the tube *h*, and is air tight. Before connecting the bulb *g*, it must be weighed with the tube *h*, and the tube of caoutchouc which unites it to the bulb *e*.

The apparatus being mounted and filled with hydrogen gas, the bulb *e* is gradually heated, increasing the heat by degrees and slowly, until it becomes red hot. To do this, an argand spirit-lamp is used. The oxydes of iron are thereby completely converted into metallic iron. The water which is formed passes through the point of the tube in the bulb *g*, into which it condenses for the most part. Another small portion of the water which remains in the state of vapour, is condensed by the chloride of calcium of the tube *h*, so that nothing escapes by the tube *i*, but the excess of hydrogen gas.

When water ceases to be produced, which is easily perceived, because no fresh drops appear at the extremity on the tube which penetrates in the bulb *g*, the heat is gradually diminished and the whole is left to cool. It is necessary to take care that the current of hydrogen gas continues to pass through the apparatus whilst cooling. When completely cold, the weight of

the iron formed in *e* is to be determined, as well as that of the water obtained, the greatest portion of which is found in *g*, whilst a small portion only has been condensed by the chloride of calcium in the tube *k*. This result might, however, be immediately obtained by weighing the two bulbs *e* and *g*, and the tube *k*. The last drop of the water produced remains engaged in the point at *g*: wherefore a small portion of the glass tube with the point should be cut with a good file behind the bulb *e*, and the bulb *g* is now weighed conjointly with the tube *k*, and the portion of the pointed tube which has been cut, and which before formed part of the bulb *e*. This tube is afterwards dried and weighed by itself. The bulb *e* is then weighed again without the portion of tube that was cut, to which the weight of the latter is afterwards added. In this manner the operator is enabled to determine what loss of weight the substance under examination has sustained by treatment with hydrogen. This loss consists of oxygen. From the weight of the bulb *g*, and of the tube *k* (after the experiment, from which that of the dried tube is deducted, the weight of the water produced is known. The quantity of oxygen which this water contained is calculated, and must exactly, or almost exactly, agree with the loss of weight which the substance has experienced in *e*, in consequence of its reduction by means of the current of hydrogen gas.

The operator might in this experiment merely determine the quantity of iron reduced in the bulb *e*; the apparatus would, in effect, be much simplified, if the weighing of the water produced were neglected. When, however, the operator wishes to draw conclusions respecting the quantity of the proto and of the peroxyde of iron contained in the analysed substance, the determination of the water produced furnishes the means of confirming the quantity of oxygen contained in the substance, from the loss of weight which it has sustained in consequence of the treatment with hydrogen.

In most cases the apparatus may be simplified by merely determining the quantity of oxygen contained in the substance

from the loss which it has undergone by treatment with hydrogen gas. In such a case the bulb *g*, and the chloride of calcium tube *h*, may be dispensed with; care must be taken only that the posterior tube, which is soldered to the bulb *e*, be somewhat long. Gradually, as the water is formed, it is driven away by the flame of a small spirit-lamp, and when the disengaged hydrogen gas inflames at the orifice of the apparatus, it is necessary to watch attentively that no particles of glass are lost, which may very well take place when the water produced touches the extremity of the tube which is red hot.

Again, the bulb *g* might be omitted and the whole of the water produced be absorbed by the chloride of calcium in the tube *h*. But in most cases the quantity of the water cannot be thus accurately determined. Such a process, besides, is applicable only when the quantity of the water produced is very small, for, if considerable, a portion of the chloride of calcium would dissolve and flow at the end *i*, which would occasion a loss of water, even by evaporation. Lastly, in a great many cases it is important also to examine the nature of the water which is produced, at any rate, it is always necessary to ascertain that it has no action upon litmus paper, for it may often turn it red or blue, which shows that the peroxyde of iron under examination was not perfectly free from foreign substances.

\* It is further necessary to take care, in this experiment, to heat the bulb *e*, as strongly as the glass can bear it. If a lower heat is employed, the peroxyde of iron is, it is true, reduced in a complete manner, but the iron reduced may have acquired the property of inflaming like a pyrophorus, when it will come in contact with the atmosphere.

It is important also to manage the experiment so that the disengagement of hydrogen be very slow in order that not only the water produced may condense in *g* and *h*, but also that all the aqueous vapour mixed with the gas disengaged from the flask *a*, may be absorbed by the chloride of calcium of the tube *d*.

If the substance contains other oxydes which cannot be

reduced by treatment with hydrogen gas, they may be found after the experiment by dissolving the substance in muriatic acid. The acid often leaves small portions of foreign bodies undissolved, the weight of which must be determined and deducted from the substance which has been operated upon.

Yet this experiment indicates only the quantity of oxygen which exists in a combination of proto and of peroxyde of iron ; but there are methods by which both the quantity of the protoxyde and that of the peroxyde of iron can be determined. These methods may even be employed when these two oxydes are accompanied by other substances, but it is necessary that the whole should be soluble in muriatic acid.

The following method is employed to determine the quantity of peroxyde of iron :—A certain quantity of the substance is weighed exactly and introduced into a capacious flask susceptible of being perfectly closed with a glass stopper. The substance may be employed in lumps, provided it may be thus easily dissolved by the muriatic acid, otherwise it must be pulverised before weighing it. The flask is then filled with carbonic acid, by means of a glass tube plunging nearly to the bottom, but taking care that it does not touch the substance about to be analysed. When the operator judges that the carbonic acid, which is heavier than atmospheric air, has displaced the latter from the flask, the tube is to be withdrawn from the flask, and the quantity of muriatic acid necessary to dissolve the substance is rapidly poured in the flask, which is then to be closed forthwith ; for greater certainty a piece of wet bladder must be tied over the stopper.

When the substance has completely dissolved, the flask is opened and quickly filled with water containing as much sulphuretted hydrogen as it can possibly take. This sulphuretted hydrogen aqueous solution must be quite recent, and must, besides, be perfectly clear and free from uncombined or deposited sulphur. The flask must then be immediately closed, and the wet bladder is again tied over the stopper. The water turns

milky, but in the course of a few days it becomes clear and sulphur is deposited.

\* The hydrogen of the sulphuretted hydrogen has converted the peroxyde of iron in the solution into protoxyde of iron, sulphur being at the same time liberated. If the liquor does not turn milky by the addition of the solution of sulphuretted hydrogen, and if no sulphur is deposited, the substance contains protoxyde of iron only, and no peroxyde of iron.

When the precipitated sulphur has deposited, the clear liquor is poured off and filtered as quickly as possible through a small filter, upon which the sulphur is washed. The contact of the air should be cautiously avoided whilst filtering in order to prevent the deposition of another portion of sulphur from the undecomposed sulphuretted hydrogen. The sulphur is dried on the filter at a very gentle heat and then weighed. It should be burnt, after weighing it, in order to ascertain whether it is pure. If the substance contained foreign bodies undissolved by the muriatic acid employed, such as, for example, a small quantity of silicic acid, they are obtained after the combustion of the sulphur, and their weight may be determined and deducted from that of the sulphur. If the quantity of silicic acid is considerable, the weight of the sulphur is determined in the manner which will be described under the article Silicium. From the weight of the sulphur obtained that of the peroxyde of iron contained in the substance under examination may be easily ascertained by means of the tables.

It is necessary in this experiment to employ a sufficient quantity of solution of sulphuretted hydrogen. The flask upon being opened must still smell distinctly of sulphuretted hydrogen. If this is not the case, the quantity of peroxyde of iron in the substance under examination was too considerable in proportion to the quantity of the sulphuretted hydrogen employed.<sup>1</sup>

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<sup>1</sup> According to Soubeiran, this determination must be performed at the ordinary temperature, for if heat were applied, some of the sulphur would redissolve, and become converted into sulphuric acid.—ED.

\* *Another method* of determining the quantity of peroxyde of iron has been indicated by Berzelius, it is as follows :—The substance is to be put into a flask capable of being closed quite tight and dissolved therein, the atmospheric air being previously driven out by means of carbonic acid as before. The solution may be promoted by a gentle heat. If any portion remains insoluble, the clear liquor is decanted, and the residuum is rapidly washed with boiling water freed from air. The whole liquid is introduced into a flask containing a weighed quantity of pulverised metallic silver and boiled with water free from air, and the flask is closed immediately.

\* The best method of obtaining the powder of silver employed in this experiment consists in pouring water, slightly acidulated, upon some fused chloride of silver, and plunging a piece of zinc in the liquor, until all the silver is reduced. The zinc is then removed, and the cake of silver obtained is washed with muriatic acid, rubbed between the fingers, and the powder thus produced is boiled with water and dried, but without heating it too much.

\* The liquor above alluded to is digested with this silver powder at a temperature of about 100° Cent. (212° Fahr.), taking care to stir it frequently. The silver reduces all the perchloride of iron into protochloride of iron, and chloride of silver is formed. When the liquor has become colourless, which requires about twenty-four hours, the clear portion is decanted, the silver is collected on the filter, it is washed and dried, and then weighed. The increase of weight indicates the quantity of chlorine taken from the perchloride of iron. By means of the tables the quantity of the peroxyde of iron contained in the substance may be calculated from the quantity of chlorine found as just said.

\* The method which Fuchs indicated to determine immediately the peroxyde of iron in a combination which contains the two oxydes of iron, is similar to that by which peroxyde of iron is separated from protoxyde of manganese by means of



*carbonate of lime*, and which has been described (page 91). If protoxyde of iron is contained in the solution, carbonate of lime does not precipitate a single trace of it.

\* When this method is resorted to, the compound of the two oxydes is dissolved in muriatic acid, out of the contact of the air, taking care to avoid an excess of acid. A sufficient quantity of carbonate of lime is then added, and the whole is heated, but not to ebullition. Whilst under the action of the heat, it is hardly possible that the atmospheric air should abandon any oxygen to the protoxyde of iron dissolved, for the carbonic acid which is disengaging impedes almost entirely its finding access to the solution. The solution having been warmed, as just mentioned, the flask is to be closed, and the peroxyde of iron precipitated is allowed to settle with the excess of carbonate of lime employed. The deposit is collected on a filter, washed rapidly with boiled water, and dissolved in muriatic acid; ammonia is then poured in the solution in order to precipitate the peroxyde of iron, taking care to operate out of the contact of the air in order to guard against the oxyde being contaminated by carbonate of lime.

\* The protoxyde of iron in the filtered liquor is determined by converting it into peroxyde of iron by means of nitric acid, and from its quantity that of the protoxyde of iron is calculated by means of the tables.

\* This method cannot be employed when the substance to be analysed contains sulphuric acid, phosphoric acid, or arsenic acid.

\* *Carbonate of baryta* is preferable by far to *carbonate of lime* for the purpose, but it must be mixed only in the cold with the solution which must not be subsequently boiled.

\* Neither can this method yield an accurate result unless great precautions be taken, because the peroxyde of iron precipitated by the carbonate of baryta or of lime is very difficult to collect on a filter, without having the quantity of that oxyde increased by a little peroxyde of iron produced by the oxydisement

of the protoxyde of iron, even though all the rules which have been laid down be attended to.<sup>1</sup>

The method of determining the quantity of protoxyde of iron in a compound which contains both oxydes, is as follows:—A given weight of the combination is to be treated as we have said in describing the preceding methods; that is to say, it is introduced in a flask susceptible of being hermetically closed, and muriatic acid is poured upon it, taking care to fill the flask previously with carbonic acid. The flask need not be as large as when the quantity of peroxyde of iron has to be determined by means of the solution of sulphuretted hydrogen. The solution being effected, some solution of potash or soda-chloride of gold is rapidly poured in the flask, which is to be immediately closed, and the whole is left for some time in a cool place, without previously heating it. The protoxyde of iron contained in the solution reduces the gold, and is converted into peroxyde of iron.

If no gold is reduced, it is a proof that the substance contains no protoxyde of iron. This, however, is still more decisively proved by adding a solution of ferricyanide of potassium to another portion of the solution, by which means the smallest portion of protoxyde of iron contained in a liquor containing large quantities of peroxyde of iron can be recognised by the production of the blue precipitate formed.

If, however, metallic gold has been deposited, it is after some time collected upon a filter, well washed, feebly ignited, and the weight is determined, from which, by means of the tables, the quantity of the protoxyde of iron may be calculated. In performing this experiment, it is necessary to avoid the contact of the air as much as possible pending the dissolving in muriatic acid, in order to avoid the conversion of protoxyde

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<sup>1</sup> According to Liebig, this absorption of oxygen does not take place when carbonate of magnesia is employed instead. M. Dübereiner separates peroxyde of iron from protoxyde of iron by means of a solution of formiate of alkali. The two oxydes are to be first dissolved in a minimum of acid, the solution is then neutralised, and by pouring into it a solution of formiate of alkali, the peroxyde of iron is precipitated in the state of basic formiate.—En.

of iron into peroxyde of iron before the addition of the solution of gold.

The same result could not be obtained by substituting the solution of perchloride of gold to that of the potash or soda-chloride of gold, because, however carefully the former may have been prepared, the gold which it contains is more easily reduced by the effect of accidental circumstances than that which exists in the crystallised potash or soda-chloride of gold, in consequence of which its solution yields less accurate results than that of the latter salt.

If the substance under examination contains a small quantity of foreign bodies insoluble in muriatic acid, they may be obtained as a residuum by dissolving the reduced gold in aqua regia; these impurities are then collected on a filter, washed, ignited, and weighed, and the weight thereof is deducted from that of the gold reduced, the exact quantity of which may now be known.

This method of determining the quantity of protoxyde of iron may be resorted to in a great number of cases, in which that for finding the quantity of peroxyde of iron could not be employed.

It has already been observed that none of these methods can be used when the substance to be analysed is not soluble in muriatic acid. In such cases it is not only impossible to determine with certainty the relative proportions of the protoxyde and of the peroxyde of iron; but very often the means are wanting of even ascertaining which of the two oxydes of iron is contained in the substance. In analysing it, the iron is obtained in the state of peroxyde. It is ordinarily admitted that the iron was contained in the state of peroxyde when the analysis yields no excess; and when an excess is found, it is looked upon as a proof of the existence of a certain quantity of protoxyde of iron in the substance. If the analysis has been carefully made, this conclusion is right when the iron is one of the principal constituents under examination; but in the contrary case, the degree of oxydisement of the iron in the substance cannot be determined. Even when the other oxydes contained

in the substance are not reducible by hydrogen gas, this mode of reduction cannot be resorted to for the purpose of determining the quantity of oxygen in the oxydes of iron, because ordinarily in the substances which muriatic acid cannot dissolve, the oxydes of iron are not susceptible of being reduced by hydrogen gas.

Neither can the operator judge of the degree of oxydisement of the iron from the colour of the substance to be analysed, at least, without a great risk of error; yet, it is customary to assume that a green or a black colour is due to the presence of protoxyde of iron, and a red, a yellow, or a white colour, on the contrary, shows the presence of peroxyde of iron. It is true, that a black colour especially when, at the same time, the substance has a strong action upon the magnetic needle, indicates the presence of protoxyde of iron, but even in that case, it may be accompanied by a great quantity of peroxyde of iron.

\* [To these methods, we must add that which has been proposed by M. Fuchs for the determination of protoxyde, and of peroxyde of iron, in the phosphates of iron.

\* A weighed quantity of phosphate of iron is dissolved in an excess of muriatic acid, and boiled with it, in order to expel all the atmospheric air from the glass matras in which the solution has been effected. A weighed blade of copper is then introduced into it, and the boiling is continued until the colour of the liquor indicates that it contains a protosalt of iron only. The copper dissolves at the expense of the oxygen of the peroxyde of iron, and is converted into subchloride of copper, which is retained in the state of colourless solution by the excess of acid. The liquor is mixed with boiled water, and the blade of copper being withdrawn, is washed with hot water, dried, and weighed. The loss corresponds to two equivalents of copper for each equivalent of oxygen taken from the peroxyde of iron, and consequently, for each equivalent of peroxyde of iron contained in the solution.

\* In order now to determine the quantity of the protoxyde of

iron, a fresh quantity of the ore is dissolved in muriatic acid, and it is brought to the maximum of oxydisation by means of a current of chlorine, the excess of which is to be expelled by boiling. A blade of copper is now plunged into it, and the operator proceeds, as has been just described.

\* By this operation, the total quantity of the iron is determined in the state of peroxyde of iron, from which, that of the protoxyde may be easily deduced.

\* It is absolutely necessary in this experiment, that the copper employed should be perfectly free from iron. M. Fuchs prepares such copper by precipitating sulphate of copper by iron, boiling the precipitate with muriatic acid, washing with water, fusing and laminating it. The blade of copper must be thoroughly scoured with muriatic acid, and then washed with water, each time before using it. The boiling should take place in a matras, with a long and narrow neck, so as to guard against the absorption of the oxygen of the air.

\* By the new processes of electrotyping, blades of copper sufficiently pure for this operation might doubtless be obtained from the decomposition of sulphate of copper by the battery.

\* Fuchs' method ceases to be rigorously accurate, when the ore contains arsenic, because this metal is then deposited in thin spangles upon the metallic copper.]<sup>1</sup>

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<sup>1</sup> This in fact is Reinch's test for the detection of arsenic. See vol. i., p. 377.

M. Marguerette proposed a method for the estimation of iron (*Comptes rendus de l'Académie*, vol. xxii.) by means of a test liquor of a known strength, and based upon the mutual reaction of the protosalts of iron upon permanganate of potash. The solution of the persalt of iron obtained is first brought to the state of protosalt of iron, and a portion of the test liquor of permanganate is added, the colour of which continues to be destroyed so long as a trace of the protosalt remains to be peroxydised; but continuing to add more of the test liquor, a time comes when the last drop added ceases to be decolorised, and imparts a pink hue to the whole liquor, which is a sign that the operation is at an end. The quantity of permanganate employed corresponds to the quantity of iron contained in the solution. The details of this method are given at length in the "*Comptes rendus*," to which the reader is referred.—Ed.

## CHAPTER XVI.

## ZINC.

## DETERMINATION OF ZINC AND OF OXYDE OF ZINC.

WHEN oxyde of zinc is contained alone in a liquor from which it has to be quantitatively determined, it cannot be done in the state of sulphate so well as for magnesia. The sulphate of zinc loses part of its acid by ignition, owing to which, a small portion of the salt can no longer be dissolved in water.

The reagent which is ordinarily used to precipitate oxyde of zinc, is solution of carbonate of *potash* or of *soda*, the latter being preferable, because carbonate of potash generally contains small quantities of silicic acid. If the solution of oxyde of zinc contains no ammoniacal salts, an excess of carbonate of alkali is poured into it, and the whole is boiled. The carbonate of zinc, which is thereby precipitated, is collected on a filter, and washed. If, on the contrary, the solution contains ammoniacal salts, they must be previously decomposed by means of the carbonate of alkali, with the help of heat.<sup>1</sup> The best way of effecting this, is to add the carbonate of alkali in sufficient quantity to decompose the ammoniacal salts, and to evaporate the whole to dryness;<sup>2</sup> a large quantity of hot water is then poured on the dry mass; the whole is boiled, and the carbonate

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<sup>1</sup> It is important to add enough carbonate of alkali to decompose entirely the ammoniacal salts which may exist in the liquor, otherwise they will prevent the precipitation of the basic carbonate of zinc.—ED.

<sup>2</sup> This evaporation to dryness should be performed in a Florence flask, inclined

of zinc is collected on a filter. The operator must be very careful not to make a mistake respecting the quantity of carbonate of alkali to be employed, and observe the same precautions which have been prescribed (page 36) in reference to the precipitation of magnesia from a solution which contains ammoniacal salts by means of carbonate of alkali. If, after having poured an excess of carbonate of alkali in a liquor which contains oxyde of zinc, the solution were evaporated to dryness slowly, and by a gentle heat, cold water poured upon the dry mass, and the carbonate of zinc collected upon a filter, the filtered liquor would still retain a great quantity of oxyde of zinc in solution, which is not the case when the liquor is dried by a strong heat, and the residuum treated as we have said.<sup>1</sup>

When oxyde of zinc is precipitated by carbonate of alkali, the operator should never omit to examine whether the liquor filtered from the carbonate of zinc contains still any oxyde of zinc. This is best ascertained by means of hydrosulphuret of ammonia. If a bulky white precipitate is thereby produced, it is a proof that oxyde of zinc is still left in solution. The small quantity of sulphuret of zinc thus produced, is treated as we have just explained. When these requisite precautions have been attended to, the quantities of sulphuret of zinc indicated by this test are imponderable.

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as in the figure, in order to avoid loss by spirting, and solution of carbonate of alkali should be added, so long as the aqueous vapour escaping from the flask has an alkaline reaction on turmeric paper, which indicates that ammonia is disengaging, and therefore that the ammoniacal salts are not yet wholly decomposed.—Ed.

<sup>1</sup> According to Dr. Fresenius, the precipitate by carbonate of alkali in a cold neutral solution is a basic carbonate of zinc, or rather a basic carbonate and hydrate of zinc,  $2 \text{ Zn O}, \text{ CO}_2 + 3 \text{ Zn O}, \text{ HO}$ , mixed with a double carbonate of zinc and potash. The formation of this precipitate is accordingly attended with evolution of carbonic acid, owing to which, as well as to the fact that the above precipitate is not quite insoluble in water, the water filtered from the precipitate, if cold, would retain a good deal of oxyde of zinc, which, however, is avoided by boiling the solution of zinc for some time before and after the addition of the alkaline carbonate, which will not only expel every trace of free carbonic acid from the liquor, but will likewise preclude the formation of the double carbonate of zinc and of alkali. The alkali is removed by washing the precipitated carbonate of zinc with boiling water.—Ed.



The carbonate of zinc<sup>1</sup> obtained is dried, and then strongly ignited in a platinum crucible upon an argand spirit-lamp, by which means the carbonic acid is expelled, and the oxyde of zinc left is weighed<sup>2</sup>.

*Hydrosulphuret of ammonia* is often employed to precipitate oxyde of zinc in the state of sulphuret of zinc. If the solution of the zinc salt be neutral, hydrosulphuret of ammonia may at once be added to it; but if it be acid, it must first be supersaturated by ammonia, which, if used in sufficient quantity, dissolves the oxyde of zinc, which is subsequently precipitated by hydrosulphuret of ammonia in the state of sulphuret of zinc insoluble in any excess of this reagent. The sulphuret of zinc separates in the form of a bulky white precipitate, which must not be filtered before it has completely settled, the clear liquor is then decanted, and the sulphuret is thrown on a filter. If this precaution be neglected, the sulphuret of zinc immediately blocks up the pores of the paper, and the filtering proceeds then extremely slowly. The sulphuret is washed with water to which some hydrosulphuret of ammonia has been added, it is taken whilst moist from the funnel and digested along with the filter in concentrated muriatic acid which dissolves it under disengagement of sulphuretted hydrogen. It is to be left thus in digestion until the odour of

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<sup>1</sup> The carbonate of zinc obtained, is a basic carbonate, and should be detached from the filter before igniting, otherwise the charcoal of the filter may volatilise a little zinc.—Ed.

<sup>2</sup> If the salt of zinc contained in the solution is in the state of a nitrate, and no other *fixed* bases are present, it may at once be determined, in the state of oxyde by evaporating the solution to dryness, and exposing the nitrate of zinc thus left to a gentle heat at first, and gradually to a bright red heat, until it ceases to lose weight. The nitric acid is thus entirely eliminated, and pure oxyde of zinc remains, which may be weighed. If the solution contains the zinc in the state of acetate, sulphuretted hydrogen may be employed to precipitate it in the state of sulphuret of zinc, but then no other acid must be present. Sulphuretted hydrogen precipitates the whole of the zinc, even though much free acetic acid may exist in the solution. The sulphuret of zinc thus obtained is afterwards digested in muriatic acid, until all odour of sulphuretted hydrogen has disappeared; the solution isedulcorated with water, filtered, and precipitated by carbonate of soda.—Ed.



sulphuretted hydrogen has almost entirely disappeared, the liquor is filtered<sup>1</sup>, and the oxyde of zinc is precipitated by carbonate of alkali.

\* According to Abich, the sulphuret of zinc precipitated may be entirely converted into oxyde of zinc, completely free from sulphuric acid by half an hour's ignition in a blast furnace in a platinum crucible, but to effect this, an exceedingly high temperature is required.

#### SEPARATION OF OXYDE OF ZINC FROM PEROXYDE OF IRON.

Oxyde of zinc is separated from peroxyde of iron, when in very small quantity compared to the latter oxyde, by means of pure ammonia, an excess of which is to be poured in the solution of the two oxydes. The oxyde of zinc remains dissolved, whilst the peroxyde of iron is precipitated. After having filtered the liquor from the precipitate, the oxyde of zinc is precipitated from the filtered solution by pouring into it carbonate of alkali and evaporating to dryness.

Yet this method can be employed only when the quantities of the two oxydes is inconsiderable, for, if more abundant, it is impossible to obtain the peroxyde of iron free from oxyde of zinc. In such a case the two oxydes are separated by means of succinate of ammonia or of soda, taking care, before adding this reagent, to neutralise the solution by ammonia, or rather to supersaturate it very slightly, so as to precipitate a small quantity of peroxyde of iron.

\* The separation of oxyde of zinc from peroxyde of iron may very well be executed by means of *carbonate of lime*, or, better still, of *carbonate of baryta*. The two oxydes are dissolved in an acid, preferably in muriatic acid, an excess of which should be avoided, after which carbonate of baryta is added in the cold,

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<sup>1</sup> Of course the filter must be thoroughly washed, in order to obtain all the chloride of zinc, and hot water is best for the purpose.—ED.

taking care to mix and stir the liquor thoroughly<sup>1</sup>. In the course of an hour, the whole of the peroxyde of iron is completely precipitated; it is then obtained separate from the excess of carbonate of baryta, in the manner which has been described, (page 92), when I spoke of the means of separating protoxyde of manganese from peroxyde of iron; the oxyde of zinc is likewise separated from the baryta in the filtered liquor, by operating as I have said for separating protoxyde of manganese.

\* In this experiment, and, in fact, in all those in which carbonate of baryta is employed, the quantity of the peroxyde of iron obtained is a little larger than it should be, because a little oxyde of zinc is carried down with it; but the quantity of the latter is very small indeed.

\* *Another method* of separating oxyde of zinc from peroxyde of iron, consists in dissolving these two oxydes in acetic acid, and passing a current of sulphuretted hydrogen through the solution. The oxyde of zinc may thus be completely precipitated in the state of sulphuret of zinc, whilst the current of sulphuretted hydrogen, traversing a solution of acetate of iron containing an excess of acetic acid, precipitates sulphur only, and no iron.

\* The difficulty of this method lies in dissolving the peroxyde of iron in the acetic acid. If it has been ignited, it is almost insoluble in acetic acid. If moist, it dissolves readily, it is true, in pretty strong acetic acid, but it often separates from such a solution in the form of a jelly even in the cold, in which case it cannot be redissolved by the addition of a fresh quantity of acid. If the liquor be heated, the peroxyde of iron is almost completely precipitated.

\* To obviate this difficulty the peroxyde of iron and oxyde of zinc are first dissolved in sulphuric acid. The solution takes place even when the oxydes have been strongly ignited, only in

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<sup>1</sup> The carbonate of baryta must be added in excess; the precipitate deposited is a basic carbonate of peroxyde of iron mixed with the excess of carbonate of baryta employed.—ED.

such a case a concentrated acid [that is mixed with equal parts of water] must be employed. This acid is poured upon the oxydes which have been ignited in a platinum capsula, and heat is applied, taking care to avoid all projection, until the water and most of the excess of sulphuric acid have evaporated. Water being now added, dissolves, with the help of heat, the white mass of sulphates formed; if a little red peroxyde of iron were left undissolved, the supernatant liquor should be decanted, and the residuum treated anew by a few drops of sulphuric acid. An excess of a solution of acetate of baryta is now poured in the solution of the sulphates without applying heat. The whole might be filtered in order to separate the sulphate of baryta precipitated, and free acetic acid being added to the filtered liquor, the peroxyde of iron and oxyde of zinc might then be separated by passing a current of sulphuretted hydrogen through the liquid. Yet, as by operating thus the collection of the sulphate of baryta upon the filter might prove difficult, because the liquor must not be heated, it is simpler, immediately after the precipitation by means of the acetate of baryta, to add free acetic acid and to pass a current of sulphuretted hydrogen through the milky liquor. The oxyde of zinc, at first, falls down with a greenish tinge, due to the presence of some particles of sulphuret of iron, but the precipitate is decolorised by heating the liquor, and again passing a current of sulphuretted hydrogen through it.

\* The precipitate is collected on a filter, washed with water to which a little solution of sulphuretted hydrogen has been added. It is digested with the help of heat and along with the filter in muriatic acid, the whole is filtered, and the oxyde of zinc is precipitated from the filtered acid liquor.

\* The solution separated from the sulphuret of zinc is treated by sulphuric acid which precipitates the baryta contained therein, and it is then heated with nitric acid in order to convert the protoxyde of iron into peroxyde, filtered in order to separate the sulphate of baryta, and the peroxyde of iron is then precipitated by ammonia.

\* It is absolutely necessary to follow exactly the course which has just been traced, and also to take care that the liquor from which the oxyde of zinc has to be precipitated by means of sulphuretted hydrogen should contain no organic acids except acetic acid, otherwise a portion of oxyde of zinc would escape being precipitated in the state of sulphuret of zinc and would remain in solution in the liquor<sup>1</sup>.

\* SEPARATION OF OXYDE OF ZINC FROM PROTOXYDE OF IRON.

When oxyde of zinc and protoxyde of iron have to be separated from each other, the operator begins by converting the latter into peroxyde of iron by heating the whole with nitric acid, and the peroxyde of iron may subsequently be separated by means of a succinate of alkali or of carbonate of baryta; or else the two oxydes are converted into acetates, and then separated by means of sulphuretted hydrogen gas. The transformation of the two bases into acetates is effected in the same manner as that which has been expounded just now; they are dissolved in sulphuric acid, and the sulphates produced are treated by acetate of baryta.

SEPARATION OF OXYDE OF ZINC FROM PROTOXYDE OF  
MANGANESE.

Oxyde of zinc may be separated from protoxyde of manganese by pure potash. Even when a large excess of solution of potash is added to that of the two oxydes and the whole is boiled for a long time, and the operator filters and washes most carefully the protoxyde of manganese, which, in the contact of the air, is partially converted into sesquioxycde of manganese, yet a small quantity of oxyde of zinc remains combined with the manganese, and cannot be removed by potash.

\* The best way of effecting the separation of these two

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<sup>1</sup> The sulphuret of zinc precipitated should have a pure white colour, otherwise some iron is present.—ED.

oxydes consists in transforming them into sulphates, pouring free acetic acid in the solution and passing a current of sulphuretted hydrogen through it. The zinc alone is precipitated in the state of sulphuret, whilst, in presence of acetic acid, the whole of the protoxyde of manganese remains in solution.

\* It is necessary that the liquor should contain no other organic acids than acetic acid. If the two oxydes are dissolved in an acid of whatever kind, but which can be expelled by sulphuric acid, the latter is to be added to the solution and evaporated to dryness; the sulphates thus formed are then dissolved and acetate of baryta and free acetic acid are added to the liquor, from which the zinc may then be precipitated in the state of sulphuret of zinc by a current of sulphuretted hydrogen. The whole is then filtered, and the protoxyde of manganese is determined in the filtered liquor, after having removed the baryta by means of sulphuric acid<sup>1</sup>.

#### SEPARATION OF OXYDE OF ZINC FROM ZIRCONIA, THE OXYDES OF CERIUM, YTTRIA, THORINA, AND GLUCINA.

Oxyde of zinc may be separated from these substances by converting them into sulphates, adding free acetic acid to the solution, and precipitating the zinc, in the state of sulphuret, by means of sulphuretted hydrogen.

#### SEPARATION OF OXYDE OF ZINC FROM ALUMINA.

These two oxydes may be separated from each other either by dissolving them in a large excess of potash, and precipitating the zinc from the solution, in the state of sulphuret of zinc, by a current of sulphuretted hydrogen<sup>2</sup>, or by converting them into

<sup>1</sup> According to Richter, oxyde of zinc may be separated from protoxyde of manganese by converting them into nitrates, calcining, and treating the residuum by concentrated acetic acid, which dissolves the oxyde of zinc only. This latter operation must be performed in the cold, and yields good results even when the quantity of the manganese is very small compared with that of the zinc.—Ed.

<sup>2</sup> That is to say, if the solution contains not only alumina and oxyde of zinc, but other substances likewise, such as iron, manganese, &c., the addition of potash will

acetates, and treating the solution [in the cold] by a current of sulphuretted hydrogen, which precipitates sulphuret of zinc. The conversion of oxyde of zinc and of alumina into sulphates, especially when these substances have been ignited, may be accomplished in the same way as that of oxyde of zinc and of peroxyde of iron, in analogous circumstances<sup>1</sup>.

\* There is, however, a native combination of alumina and oxyde of zinc, called *Gahnite*, which is insoluble in acids. This mineral resists also the action of carbonate of potash, when submitted to fusion with this substance. It cannot be rendered soluble in acids, except by fusion with pure potash, or by strong ignition with carbonate of baryta. The treatment of this mineral by potash is the same as that of silicious compounds by potash or baryta. The course to be adopted will be described farther on, when we come to speak of silicious substances.

#### SEPARATION OF OXYDE OF ZINC FROM MAGNESIA.

Oxyde of zinc is separated from magnesia in the same manner as protoxyde of manganese is separated from this earth. Muriate of ammonia is added to the solution in sufficient quantity to prevent the ammonia which is subsequently added from precipitating either oxyde of zinc or magnesia; but this need not be done when the liquor is acid, because, by saturating it with ammonia, enough ammoniacal salt is produced. Hydro-sulphuret of ammonia is then poured in the solution, in order to precipitate the zinc in the state of sulphuret of zinc. The liquor filtered from this precipitate is then rendered acid, heated, and, after filtering it again, the magnesia may be separated.

\* Magnesia may also be separated from oxyde of zinc by

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precipitate the whole, but by putting a large excess of potash and boiling, the oxyde of zinc and alumina only will be redissolved, and must be separated from the other insoluble substances by filtering and washing, from which solution a current of sulphuretted hydrogen will precipitate the zinc as described.—En.

<sup>1</sup> Oxyde of zinc may also be separated from alumina by cyanide of potassium, which precipitates the latter in the state of hydrate of alumina, insoluble in an excess of the reagent.—En.

means of *sulphuretted hydrogen*, after having previously converted the two bases into acetates. The course to be followed is the same as we have described for separating oxyde of zinc from protoxyde of manganese from their acetic acid solutions, by sulphuretted hydrogen <sup>1</sup> (page 121).

#### SEPARATION OF OXYDE OF ZINC FROM LIME.

Oxyde of zinc may be separated from lime in the same manner as for separating lime from magnesia. The solution is to be rendered ammoniacal, and the lime is precipitated therefrom by oxalate of ammonia. The oxalate of zinc is not precipitated, because the ammonia retains it in solution. Carbonate of potash is then poured in the liquor filtered from the oxalate of lime produced, and evaporated to dryness by a strong heat : carbonate of zinc is thus obtained.

Lime might also be separated from oxyde of zinc by pouring ammonia in the solution of these two substances, and subsequently adding hydrosulphuret of ammonia to the liquor, by which means the zinc is precipitated in the state of sulphuret of zinc. The precipitate thus formed should then be filtered as rapidly as possible out of the contact of the air, in order to avoid its being contaminated by carbonate of lime ; and as time cannot be allowed for the sulphuret of zinc to be deposited, it should be precipitated in a flask capable of being corked up, in order to prevent the access of the atmospheric air. The sulphuret produced is then allowed to settle before filtering. The liquor filtered therefrom is rendered acid and heated ; it is then filtered again, and the lime is precipitated from it in the usual way.

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<sup>1</sup> According to Dr. Fresenius and Haidlen, oxyde of zinc may also be separated from magnesia by means of carbonate of potash or of soda. Cyanide of potassium is then added in sufficient quantity to redissolve the zinc. The mixture is evaporated to dryness, more carbonate of alkali is added, the whole is again evaporated to dryness, and the dry residuum is treated by water, which dissolves the zinc in the state of double cyanide of zinc and of potash, whilst the magnesia remains insoluble.—Ed.

When the lime and oxyde of zinc can be converted into acetates, they may be separated from the acetic acid solution by sulphuretted hydrogen, which precipitates the zinc in the state of sulphuret. The conversion of the two oxydes into acetates is effected by precipitating them by a carbonate of alkali in the state of carbonates, which may then be dissolved by acetic acid.<sup>1</sup>

#### SEPARATION OF OXYDE OF ZINC FROM STRONTIA.

Strontia may be separated from oxyde of zinc in the same manner as lime, yet only one of the two methods mentioned should be resorted to, that by oxalate of ammonia is inapplicable.<sup>1</sup>

#### SEPARATION OF OXYDE OF ZINC FROM BARYTA.

Baryta is separated from oxyde of zinc by means of sulphuric acid, which precipitates the baryta. The liquor is filtered, and the zinc is then separated from it in the usual way<sup>1</sup>.

#### SEPARATION OF OXYDE OF ZINC FROM THE ALKALIES.

Oxyde of zinc is separated from the fixed alkalies as follows : The solution is first rendered ammoniacal, and the zinc is precipitated in the state of sulphuret of zinc by means of hydrosulphuret of ammonia. The filtered liquor is then rendered acid, heated, filtered, evaporated to dryness, and the dry residuum is ignited ; the alkalies remain combined with the acid to which they were united before their separation, provided always that

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<sup>1</sup> According to Messrs. Fresenius and Haidlen, oxyde of zinc may be separated from lime, baryta, and strontia, by cyanide of potassium, as mentioned in the note before (*Annal. der Chem. und Pharm.* Bd. xliii. hef. 2), that is to say, a slight excess of carbonate of potash is added to the solution, then cyanide of potassium, and the whole is heated ; the earthy carbonates remain insoluble, whilst the carbonate of zinc is thereby dissolved with the greatest ease. The whole is filtered, and the filtrate, to which muriatic acid is added, is boiled, adding gradually some nitric acid until all the hydrocyanic acid is eliminated. The zinc is afterwards precipitated by means of carbonate of soda, with the usual precautions.—Ed.



the salt of which they consist is not one capable of being decomposed by heat.

\* When the alkalies and oxyde of zinc can be converted into acetates, a current of sulphuretted hydrogen is then passed in the solution of these acetates, by which means the zinc is precipitated in the state of sulphuret of zinc.

## CHAPTER XVII.

## COBALT.

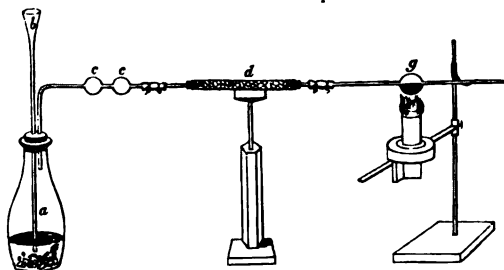
## DETERMINATION OF COBALT AND OXYDE OF COBALT.

SOLUTION of pure *potash* is the best reagent for precipitating oxyde of cobalt from its solutions. The precipitate is bulky, and consists of a basic salt, having a blue colour, which in the course of a short time becomes green. It is advisable to precipitate the oxyde whilst hot, or else to apply a gentle heat after the precipitation; the colour of the precipitate is thereby changed, and becomes of a dirty pink colour by a prolonged ebullition. The hydrate of cobalt is then pure. This precipitate is difficult to wash, and on that account it is best to use hot water. After washing, it is dried and ignited, which renders it black, and then weighed.

Yet when this method is adopted, it is impossible to determine the quantity of the oxyde of cobalt in an exact manner, especially if at all considerable. After having several times ignited the oxyde, different weights are obtained each time, and the quantity of oxyde is always found greater than it should be. The reason of this discrepancy is, that during the ignition, or rather during the cooling of the mass, it passes into a higher state of oxydisation, which obstacle cannot be avoided, even by cooling it rapidly in a covered crucible.

In order, therefore, to determine with precision the quantity of cobalt contained in the ignited oxyde, the best is to weigh a certain quantity, to convert it into cobalt by means of hydrogen

gas, and to calculate from the weight of the metal the total quantity of the oxyde. The reduction is effected very easily in the following manner :—The flask contains zinc and water, and sulphuric acid is poured into it through the funnel *b*, in order to



produce a slow current of hydrogen gas. The hydrogen gas escapes through a glass tube bent at right angle, and provided with two bulbs *c c* into which the greatest portion of the moisture of the gas condenses ; in order, however, to dry it completely, it passes through another glass tube *d*, filled with chloride of calcium, and thence into the glass bulb *g*, containing the oxyde of cobalt ; on each side of this bulb, which must be made of strong and difficultly fusible glass, two tubes of glass are soldered. This bulb *g*, is first weighed empty, and then after having introduced the oxyde and cleaned the tubes with the feather of a pen, in order to remove the particles which might have adhered to them, it is weighed again, in order to know the exact weight of the oxyde operated upon. The various parts of the apparatus are connected by tubes of Indian-rubber.

When the whole apparatus is filled with hydrogen, the operator begins by gently heating the bulb containing the oxyde of cobalt<sup>1</sup>. The heat is then gradually increased until the bulb becomes red hot. A strong red heat is absolutely

<sup>1</sup> Care must be taken that the apparatus is quite filled with hydrogen gas before beginning to apply heat to the bulb, else an explosion may take place. This disengagement of hydrogen should, therefore, proceed for some time ; or it is better still to receive the gas which is disengaging into a tube closed at one end, suspended over the exit tube, and to test whether this tube, closed at one end, is filled with hydrogen gas, by bringing a lighted paper to its orifice.—ED.

necessary, because, unless this is attended to, the cobalt reduced would become pyrophoric and therefore would spontaneously inflame in contact with the air. Water is produced, a portion of which escapes with the excess of the hydrogen, but another portion condenses into small drops in the tube next after the bulb *g*, from which it is expelled by means of a small spirit-lamp. When water ceases to be produced, it is a sign that the whole of the oxyde of cobalt is converted into metal; the heat is then withdrawn from the bulb, but the current of the hydrogen gas continues to be passed upon the regulus whilst cooling.

\* After complete cooling, the bulb *g* is weighed, with the reduced cobalt. Before weighing it, the bulb must be held as much inclined as possible without spilling the metal which it contains. This bulb, before the reduction of the oxyde, was full of atmospheric air, but after the reduction it contains hydrogen gas which would render it lighter were not this gas to be replaced by atmospheric air. The weight indicates the quantity of the metal existing in that of the oxyde operated upon, the difference between the two last weighings shows the quantity of the oxygen contained in the oxyde of cobalt. From the weight of the metal and of the oxygen the quantity of both in the whole mass of the oxyde, which could not be submitted to the reductive process, is calculated. If the cobalt was in the state of oxyde in the substance analysed, its quantity is calculated from that of the metal obtained.

When the oxyde of cobalt submitted to the reductive process has not been well washed and contains foreign substances, such, for example, as alumina, the metal reduced is pyrophoric, and inflames spontaneously however strongly it may have been ignited<sup>1</sup>.

A solution of *carbonate of potash*, even when boiled with solutions of oxyde of cobalt free from ammoniacal salts, does not completely precipitate the oxyde of cobalt therefrom as is the case with pure *potash*; but when proper care is taken, this

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<sup>1</sup> The reduced oxyde of cobalt must always be strongly ignited, otherwise it will catch fire on coming in contact with the air, however pure it may be.—ED.

latter reagent precipitates the oxyde of cobalt so completely that hydrosulphuret of ammonia fails in showing the slightest trace of it in the filtered liquid.

If the liquor from which oxyde of cobalt has to be precipitated, contains any free ammonia, or salts of ammonia, the oxyde cannot be precipitated by potash. It is true, that the solution may be mixed with a sufficient quantity of carbonate of potash and that the salts of ammonia may then be gradually destroyed by evaporating the liquor, but this method, especially when the ammoniacal salts are abundant, is somewhat complicated, and does not give accurate results, even though the liquor be evaporated to dryness, for oxyde of cobalt is not completely precipitated by the carbonate of alkalies, and, by evaporation to dryness, it is converted into peroxyde of cobalt (*suroxyde de cobalt*).

It is therefore preferable, and more expeditious in such cases to precipitate the oxyde of cobalt in the state of sulphuret by means of hydrosulphuret of ammonia. The solution of the oxyde must be neutral, it may also be rendered ammoniacal, for sulphuret of cobalt is completely insoluble in the free alkalies<sup>1</sup>. Sulphuret of cobalt forms a black precipitate, which is less voluminous than that of sulphuret of iron, and does not oxydise so easily in contact with the air. The water used to wash it must contain a little hydrosulphuret of ammonia, which is preferable to pure water.

The quantity of cobalt contained in the sulphuret of cobalt, may be determined as follows:—The sulphuret of cobalt is scraped as well as possible from the filtering paper, and put, whilst still moist, in a glass. The filter is burnt upon the cover of a platinum or porcelain crucible, and the ashes are put in the glass along with the precipitated sulphuret. The sulphuret is then digested, with the help of heat, into nitric acid, or aqua regia, until all the cobalt has dissolved, and nothing remains

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<sup>1</sup> Sulphuret of cobalt is likewise insoluble in sulphurets of alkalies; exposure to the air gradually converts it, in the moist state, into sulphate of protoxyde of cobalt. — Klap.

but sulphur of a very pure yellow colour. Muriatic acid alone cannot decompose sulphuret of cobalt. The solution is then diluted with water, filtered, and the residuum is washed, the oxyde of potash is then precipitated by solution of potash. The oxyde thus obtained is ignited and weighed. Part of it is to be reduced by means of hydrogen gas, and from the quantity of the metal obtained, that of this same metal in the precipitate of oxyde of cobalt is determined.

\* The filter should not be digested with the sulphuret of cobalt in the nitric acid or aqua regia, because these acids react on the paper, and would thus introduce a sufficient quantity of organic matter in the solution to impede the complete precipitation of the oxyde of cobalt by potash.

DETERMINATION OF PEROXYDE OF COBALT (SESQUIOXYDE OF COBALT) [*suroxyde de cobalt*].

Peroxyde of cobalt is reduced, like the protoxyde, into metallic cobalt, when exposed at a high temperature to a current of hydrogen gas. If mixed with the other oxydes, from which it cannot be separated, except when in solution, the substance must be dissolved in muriatic acid. By heating it for a long time with this acid, the peroxyde (*sesquioxysde*) of cobalt becomes converted into chloride of cobalt under disengagement of chlorine. The oxyde of cobalt is afterwards precipitated from the solution by means of solution of potash.

\* The separation of oxyde of cobalt from other substances, is often attended with numerous difficulties, and there are several substances from which it cannot be separated with much precision.

\* In order to determine the composition of peroxyde of cobalt, Winkelblech employs oxalic acid, which is a pre-eminently valuable reagent for the analysis of peroxydes in general. Peroxyde of cobalt is converted by it into oxalate of cobalt, which is not very hygroscopic. It is necessary, however, that the peroxyde should be reduced into very fine powder. (Oxalate

of cobalt contains 2 atoms of water, and 40·9 per cent of protoxyde of cobalt) [sesquioxyde].

SEPARATION OF OXYDE OF COBALT FROM OXYDE OF ZINC.

Oxyde of cobalt cannot be separated from oxyde of zinc by solution of pure potash, even by boiling the two oxydes in a large excess of this reagent. Oxyde of zinc is indeed dissolved by this treatment, but the oxyde of cobalt which remains undissolved, always retains a great quantity of the oxyde of zinc which cannot be taken up by any excess of potash whatever.

\* The best method of separating the two oxydes from each other, consists in converting them both into acetates from the solution of which the zinc may be precipitated in the state of sulphuret by means of sulphuretted hydrogen. The oxyde of cobalt remains in solution, provided the solution contains a sufficient quantity of free acetic acid, for sulphuretted hydrogen precipitates cobalt completely in the state of sulphuret of cobalt, from a neutral solution of acetate of cobalt. It is necessary that the solution should contain no other acid than acetic acid, because, in presence of an inorganic acid, zinc is not precipitated completely by sulphuretted hydrogen.

\* The best way of converting the two oxydes into acetates, is the same as I have indicated, (page 120), whilst treating of the means of separating oxyde of zinc from protoxyde of manganese.

\* [Berzelius recommends the following method, as being very accurate; it is employed by him for separating completely oxyde of zinc from oxyde of cobalt, and oxyde of nickel. This method can, of course, be resorted to for separating oxyde of zinc, when mixed with only one of these oxydes :—

After having separated the greatest portion of the oxyde of zinc by boiling the mixture with a solution of caustic potash, the residuum is washed with cold water, and then with boiling water, until all the potash is removed. The oxyde is heated to redness, and weighed. It is then intimately mixed in a platinum crucible, with pulverised sugar. [Such as will leave no ashes

after ignition.] (Berzelius advises the operator to take the crystals of sugar deposited from an alcoholic solution ; but the sugar-candy of commerce, when chosen in perfectly defined and colourless crystals, leaves no appreciable trace of ashes.)

\* The sugar is carefully carbonised ; the porcelain crucible with the cover on, is put in a hessian crucible, and the space between the two crucibles is filled up with caustic magnesia, the latter crucible, also covered over, is exposed for one hour in a wind furnace to the strongest heat possible. The oxydes are reduced by this treatment ; the cobalt and the nickel remain in the state of carburets, and the zinc volatilises completely. The two metals left behind are dissolved in nitric acid, and the solution is evaporated to dryness in the water-bath in a counterpoised platinum crucible, the residuum is ignited to bright redness, and the oxyde is weighed. The loss of weight indicates the quantity of oxyde of zinc expelled.

\* One of the principal conditions of success in this experiment is, that the mixture of the oxydes be perfectly washed before being ignited, for, if it still contains potash, the latter acts upon the porcelain crucible ; it is advisable to test by boiling water, whether the oxydes, after having been ignited, and before being mixed with sugar, contain potash, because, should any be left, it might, as yet, be eliminated by a renewed washing.

\* It is probable that unglazed porcelain crucibles only can be used for the reduction of these oxydes, because the glazing of the porcelain would fuse at the high temperature which it is necessary to give to the mixture in order to volatilise the zinc completely.<sup>1</sup>

\* M. Ullgren proposed another method, which is as follows :—  
The solution of the oxydes of zinc, of cobalt, and of nickel,

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<sup>1</sup> For separating protoxyde of manganese from oxyde of zinc in a liquor which contains a large proportion of sal ammoniac, M. Otto adds ammonia, which produces no precipitate, and he then passes a stream of sulphuretted hydrogen, which precipitates both metals in the state of sulphurets, to which acetic acid being added, the sulphuret of manganese is thereby dissolved, whilst the sulphuret of zinc is left in an insoluble state.—Ed.





## SEPARATION OF OXYDE OF COBALT FROM PEROXYDE OF IRON.

The separation of oxyde of cobalt from peroxyde of iron, is effected by the same processes employed for separating peroxyde of iron from protoxyde of manganese. To the solution of the two oxydes, especially if the amount of the peroxyde of iron is small, muriate of ammonia is added, which, if in sufficient quantity, prevents the oxyde of cobalt from being precipitated by ammonia. If the solution is very acid, the addition of muriate of ammonia may be dispensed with. The liquor is then saturated with ammonia, observing the same precautions as have been described, (page 87), after which, the peroxyde of iron may be precipitated by means of a neutral succinate of alkali, and the precipitated persuccinate of iron is treated as we said before. The quantity of the oxyde of cobalt contained in the liquor filtered from the persuccinate of iron, is determined by means of hydrosulphuret of ammonia, which precipitates it in the state of sulphuret of cobalt, which is then treated as we said before.

The two oxydes may often be separated by ammonia only, but in that case, a very large proportion of muriate of ammonia must be added to the liquor, which, however, may be dispensed with, if the liquor be very acid. This method of precipitating the peroxyde of iron by ammonia, instead of succinate of ammonia, and of thus separating it from oxyde of cobalt, is especially applicable when its quantity is very feeble compared to that of the latter ; but it is far from being as accurate as the other method.

\* Neither of the two methods yields peroxyde of iron perfectly free from all traces of oxyde of cobalt, the presence of which may be demonstrated by the blowpipe.

\* The method of separating oxyde of cobalt, and peroxyde of iron, by *carbonate of baryta*, is less applicable than when the matter is to separate peroxyde of iron from other oxydes. When the solution of the two oxydes is treated in the cold by an excess of carbonate of baryta, some oxyde of cobalt is precipitated

along with the peroxyde of iron, in too large quantity to be neglected even in such analyses as do not require a high degree of precision.

\* Scherer indicated a method of separating oxyde of cobalt from peroxyde of iron, which is grounded upon this; that the neutral or basic persalts of iron are precipitated from their solutions by heat or ebullition, a property which had before him been turned to account by Herschel. This method consists in dissolving the two oxydes in sulphuric acid, or in muriatic acid, or in a mixture of the two acids. The presence of nitric acid must be avoided. Solution of hydrate of potash is then added, taking care to stir at the same time, until it has only a feeble acid reaction upon litmus paper. In order not to go beyond this, a dilute solution of potash is used towards the end. If too much alkali were poured in, so that the liquor should not have an acid reaction, a sufficient quantity of acid should be added to restore, after stirring well, the acid reaction; but the quantity of the acid should not be great enough to redissolve all the precipitate.

\* By this partial saturation, the iron is precipitated in the state of a basic salt. The feeble acid reaction serves the purpose of showing that all the peroxyde of iron is not precipitated, since the neutral sulphate and the chloride of cobalt have no reaction upon litmus paper. If the saturation has been managed as I have said, the solution contains only a small quantity of peroxyde of iron, whilst not a single atom of oxyde of cobalt has as yet been precipitated. The solution is diluted with water, and it is boiled along with the precipitate which has been already produced. The boiling needs not be continued for a long time, for as soon as it begins, the last traces of iron are precipitated in the state of basic salt. The hot solution is filtered, and the basic salt of iron is washed with boiling water. The oxyde of cobalt is precipitated from the filtered liquor by means of hydrate of potash in the usual way.

\* In order to determine the peroxyde of iron as such, it is to

be drenched with ammonia whilst on the filter, owing to which, after washing, it is completely free from acid.

\* The presence of nitric acid must be avoided in this process, because the basic nitrate of iron (*nitrate ferrique*) is more soluble than the other basic persalts of iron.

\* The separation of the oxydes may also be effected by means of ammonia; yet it is impossible, in presence of ammonia, to employ a solution of hydrate of potash for the purpose of separating oxyde of cobalt from the filtered liquor.

#### SEPARATION OF OXYDE OF COBALT FROM PROTOXYDE OF IRON.

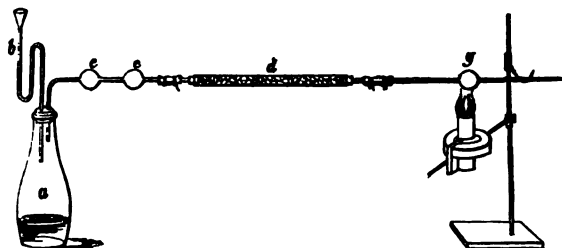
When protoxyde of iron has to be separated from oxyde of cobalt, the former should first be converted into peroxyde of iron either by nitric acid, or by a current of chlorine gas, if the solutions are acid and dilute.

#### SEPARATION OF OXYDE OF COBALT FROM PROTOXYDE OF MANGANESE.

It is very difficult to separate oxyde of cobalt from protoxyde of manganese. It can be done only by converting the two oxydes into metallic chlorides, and treating them in that state by hydrogen gas, by which the chloride of cobalt is reduced into metallic cobalt under disengagement of muriatic acid gas, whilst the protochloride of manganese remains unaltered.

The two oxydes are first precipitated together, which may be done by means of a solution of pure potash, if the liquor contains no ammonia or ammoniacal salts. When it contains these substances, an excess of carbonate of potash must be poured in the solution, and the whole evaporated to dryness. It may also be done, and better, by precipitating the two oxydes from the neutral or ammoniacal liquor by means of hydrosulphuret of ammonia, and decomposing the sulphurets produced by means of nitric acid, from which nitric acid solution the two oxydes may then be precipitated by pouring a solution of potash therein.

The oxydes are washed, ignited, and weighed, a convenient quantity thereof is then introduced in a glass bulb, to which a glass tube has been soldered on each side, and whilst the bulb is heated a current of muriatic acid gas is passed over them in order to convert them into metallic chlorides. The muriatic acid is disengaged from a flask similar to that represented (page 128), with this difference, that chloride of sodium is introduced in the flask *a*, and the sulphuric acid is poured gradually in the funnel, so as to fall only in drops in the flask, otherwise the disengagement of muriatic acid gas might proceed too violently, and determine the formation of a froth which might pass over into the tube. The funnel should be bent in order to prevent the escape of the gas that way.



The gas is dried by passing it through the glass tube *d*, full of chloride of calcium, whence it passes over the oxydes contained in the bulb *g*, heated with a spirit-lamp, in order to convert them into metallic chlorides. But a long time is required for their complete conversion, wherefore it would be much more advantageous to effect this by dissolving the oxydes in muriatic acid, but it is not possible to introduce an exact quantity of such chlorides into a glass bulb.

When the conversion of the oxydes into metallic chlorides is accomplished, the flask *a* is replaced by another containing zinc and sulphuric acid, for the purpose of disengaging hydrogen, which gas passes over the chlorides in the bulb which must be strongly heated in the mean time. The current must be stopped only when nearly all disengagement of muriatic gas has ceased. We say nearly all, because, even after the complete reduction of the

chloride of cobalt, extremely minute traces of muriatic acid continue to be exhaled from the protochloride of manganese which are not reduced by hydrogen gas, but which attack glass under the influence of a strong heat. Consequently as soon as only an almost imperceptible cloud is formed by holding a glass rod moistened with ammonia at the extremity of the apparatus, the bulb is allowed to cool, yet continuing the disengagement of hydrogen gas until the bulb has become quite cold.

When this has taken place, the bulb is put in water, which dissolves the protochloride of manganese and leaves the metallic cobalt in a state of extreme division. Yet the protochloride of manganese does not completely dissolve; brown flocks of it remain in the solution, which augment when it is left exposed for a long time to the atmospheric air; but a few drops of muriatic acid are sufficient to dissolve them. As they remain suspended in the liquid longer than the metallic cobalt, they may be decanted with the solution of the protochloride of manganese; or water previously rendered slightly acid by means of a few drops of very dilute muriatic acid is poured upon the cobalt; this water dissolves completely the traces of manganese which might still remain, but does not attack the cobalt; it is promptly decanted, and the metal is again washed, but with pure water. It may then be collected upon a weighed filter and rapidly dried at a moderate heat and again weighed. For the sake of greater certainty, a portion is weighed and heated in hydrogen gas as was said (page 128). The solution of protochloride of manganese is then treated by carbonate of potash, as we said before (page 69), which produces a precipitate of carbonate of manganese (*carbonate manganoux*).

Döbereiner gives the following method of separating cobalt from manganese. The two metals are converted into chlorides which are to be dissolved in anhydrous alcohol to which saturated solution fifteen or twenty times its volume of ether are added for the purpose of precipitating the chloride of manganese in the state

of a powder, whilst that of cobalt remains in solution; the blue supernatant liquor is decanted, and the pulverulent precipitate left at the bottom is dissolved in the smallest possible quantity of anhydrous alcohol, and the solution is again mixed with a large proportion of ether. In this way all the adhering chloride of cobalt is dissolved, and after repeating the process two or three times the chloride of manganese remains pure. It is necessary to employ ether free from alcohol for precipitating the chloride of manganese, and always to leave the mixture at rest for six or twelve hours before separating the liquor containing the dissolved chloride of cobalt<sup>1</sup>.

#### SEPARATION OF OXYDE OF COBALT FROM ALUMINA.

Oxyde of cobalt may be separated from alumina by solution of pure potash, by which it is precipitated whilst the earth remains in solution.

#### SEPARATION OF OXYDE OF COBALT FROM MAGNESIA.

The best method of separating oxyde of cobalt from magnesia is as follows:—To the solution of the two oxydes, enough muriate of ammonia is added to prevent the ammonia, which is subsequently poured in, from precipitating either of the two

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<sup>1</sup> Dr. Fresenius separates oxyde of cobalt from protoxyde of manganese by means of cyanide of potassium as follows:—Cyanide of potassium is added to the acid solution of the oxydes in question, which produces a precipitate of protocyanide of cobalt, and of protocyanide of manganese; cyanide of potassium is now added in excess, which redissolves the protocyanide of cobalt and partially the protocyanide of manganese. The whole is thrown on a filter and the precipitate is washed. The filtrate is heated to ebullition, muriatic acid being at the same time gradually poured in, in drops, and in small quantity, so as not to render the solution acid, and after which the manganese and the cobalt contained in the solution may be separated from each other, as was described before.

According to M. Cloëz (*Journal de Pharmacie et de Chimie*, vol. vii.), oxyde of manganese may be separated from oxyde of cobalt by digesting their hydrates in a solution of sulphuret of calcium saturated with sulphur,  $\text{Ca S}_2$ , by which sulphuret of cobalt, which remains dissolved in the liquor, and sulphuret of manganese which remains insoluble, are produced.—Ed.

oxydes. This addition of muriate of ammonia may be dispensed with when the liquor is acid. Hydrosulphuret of ammonia is now added to the liquor, and the sulphuret of cobalt precipitated thereby is collected on a filter, and washed with water containing a little hydrosulphuret of ammonia. The quantity of cobalt contained in this precipitate may be determined by treating it as we said before. As to the liquor filtered from the sulphuret of cobalt produced, the excess of hydrosulphuret of ammonia which it contains is first destroyed by an acid, and the magnesia which it holds in solution may be then easily determined as usual.

\* It must be remarked however that, according to Berzelius, this separation is not quite so exact as is usually thought, for a little sulphuret of magnesium is often precipitated along with the sulphuret of cobalt, especially when the hydrosulphuret of ammonia does not contain an excess of sulphur or of sulphuretted hydrogen. After having converted the sulphuret of cobalt into oxyde of cobalt, the presence of magnesia may be very easily overlooked in it. It is well therefore to dissolve the oxyde of cobalt into nitric acid, to evaporate the solution to dryness, and to expose the dry residuum to a temperature which must not exceed a red heat; peroxyde of cobalt is thus obtained, and the magnesia may be extracted by means of dilute sulphuric acid, or by nitric acid. The latter acid is preferable, because it is then necessary only to evaporate the solution to dryness, and to ignite the residuum to obtain the magnesia in a pure state. Yet this method of analysis is not complete, and it is difficult to obtain all the magnesia contained in the oxyde of cobalt without, at the same time, dissolving a little of the latter.

\* When the oxyde of cobalt and the magnesia can be obtained in the state of neutral acetates, they may be separated from each other in the dilute solution by sulphuretted hydrogen gas. If no free acetic acid exists in the liquor, the oxyde of cobalt may be pretty completely separated in the state of sulphuret, and the magnesia remains in solution.



The French edition contains the following remarks by M. E. Peligot.

“ According to M. Ullgren, magnesia is separated from oxyde of cobalt and from oxyde of nickel in the following manner:— The solution of the three oxydes is precipitated by a mixture of chlorite of potash [hypochlorite of potash], and of caustic potash. The oxydes of cobalt and of nickel are precipitated in the state of hyperoxydes mixed with hydrate of magnesia. The precipitate is washed and digested whilst still moist with a solution of protochloride of mercury in excess [corrosive sublimate] at a temperature of from 30° to 40° centigrade, [from 86° to 104° Fahr.] A double compound of chloride of magnesia and of mercury is thus formed<sup>1</sup>; the magnesia dissolves, and a proportionate quantity of basic protochloride of mercury precipitates in its stead. The solution and the water of the washings is evaporated to dryness in a counterpoised platinum crucible, the heat is increased in order to expel the chloride of mercury, and the residuum is drenched with pure nitric acid which is afterwards evaporated to dryness in the water-bath. When the nitrate of magnesia is dry, it is ignited, and the magnesia is weighed. The oxydes of cobalt and of nickel are also ignited in order to expel the mercury, and they may then be separated from each other in the ordinary manner.

#### SEPARATION OF OXYDE OF COBALT FROM LIME.

Oxyde of cobalt is separated from lime by means of oxalate of ammonia. To the solution of the two oxydes, enough muriate of ammonia is added to prevent the ammonia, which is subsequently added, from precipitating the oxyde of cobalt. This addition of muriate of ammonia may, however, be dispensed with when the liquor is acid. The lime is then precipitated by oxalate of ammonia, and the oxyde of cobalt may now be precipitated from the filtered liquor in the way which has been exposed before. It is necessary, however, to filter the oxalate of

<sup>1</sup> The composition of this double salt is as follows :  $\text{Mg. Cl.}, 3 \text{ Hg. Cl.}$ —Ed.

lime very rapidly, and to avoid the contact of the air as much as possible, in order to guard against the oxyde of cobalt in the ammoniacal liquor absorbing any oxygen.

As oxyde of cobalt requires a large quantity of ammonia for its solution, this method cannot be strongly recommended, although it is the one generally employed. A more accurate result is obtained as follows:—To the ammoniacal solution of the two substances, hydrosulphuret of ammonia is added, which precipitates the oxyde of cobalt in the state of sulphuret of cobalt. The liquor is rapidly filtered, and as much as possible out of the contact of the air, in order to prevent contamination with carbonate of lime, and the precipitate is washed with water containing some hydrosulphuret of ammonia. Taking now the liquor filtered from the sulphuret of cobalt, the excess of hydrosulphuret of ammonia is destroyed by pouring muriatic acid into it, and the lime is then precipitated. It is advisable to use a flask capable of being corked or stoppered, in order to allow time for the sulphuret of cobalt to settle well, and to filter only after the complete settling, in order that the lime contained in the solution may traverse the filter before carbonate of lime has time to form.

#### SEPARATION OF OXYDE OF COBALT FROM STRONTIA.

Oxyde of cobalt is separated from strontia in the same manner as for separating it from lime. This separation might also be effected by means of sulphuric acid.

#### SEPARATION OF OXYDE OF COBALT FROM BARYTA.

Oxyde of cobalt is separated from baryta by means of sulphuric acid. The liquor is filtered from the sulphate of baryta thus formed, and the oxyde of cobalt is precipitated by pure potash<sup>1</sup>.

<sup>1</sup> According to MM. Haidlen and Fresenius, cobalt may be separated from lime, strontia, and baryta, by adding an excess of cyanide of potassium to the acidified solution of the bases, heating the mixture, and adding a solution of carbonate of potash, the cobalt is thus dissolved in the state of double cyanide of cobalt and of potash, which may be separated by filtering from the insoluble earthy carbonates.—Ed.

**SEPARATION OF OXYDE OF COBALT FROM THE ALKALIES.**

In order to separate oxyde of cobalt from the alkalies, hydrosulphuret of ammonia is added to the neutral or ammoniacal solution, by which a precipitate of sulphuret of cobalt is produced. The hydrosulphuret of ammonia in excess in the filtered liquor is destroyed by means of an acid, after which the quantity of alkali contained in it may be determined in the usual way.

## CHAPTER XVIII.

## NICKEL.

## DETERMINATION OF NICKEL AND OF OXYDE OF NICKEL.

As for oxyde of cobalt, so is a solution of pure *potash* the best reagent for precipitating oxyde of nickel from its solutions. A bulky apple-green precipitate is thus formed which consists so entirely of oxyde of nickel [*hydrate of protoxyde of nickel*] that not the slightest trace of this oxyde can be detected in the liquor filtered from the precipitate, provided the necessary precautions have been attended to, and especially by heating the whole. The precipitate is difficult to wash, and hot water should therefore be employed for the purpose,<sup>1</sup> after which it is dried, ignited, and weighed. Ignition renders it black, and it then consists of pure oxyde of nickel, the weight of which is not altered by repeated ignition and cooling. The use of hydrogen gas is not, therefore, necessary to reduce this oxyde, which, on the contrary, cannot be dispensed with for oxyde of cobalt.

The precipitation of oxyde of nickel must always be effected by caustic potash, because it is not completely precipitated by carbonate of potash or of soda.

Pure potash precipitates oxyde of nickel completely even in the cold, not only from solutions which contain muriate of ammonia or other ammoniacal salts, but also from solutions which contain free ammonia. This behaviour with potash is

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<sup>1</sup> See my filtering apparatus, page 33.

eminently characteristic for distinguishing oxyde of cobalt from oxyde of nickel.

*Hydrosulphuret of ammonia* does not precipitate oxyde of nickel so well as it does oxyde of cobalt from neutral solutions, or from solutions which have been rendered ammoniacal, because sulphuret of nickel is a little soluble in an excess of this reagent,<sup>1</sup> with which it forms a brown solution, which, in the concentrated state, is perfectly opaque. By evaporating such a solution, a portion of sulphuret of nickel is, according to Berzelius, precipitated, but another portion is converted into oxyde, and remains dissolved<sup>2</sup>.

The best way of precipitating oxyde of nickel in the state of sulphuret of nickel, from its neutral or ammoniacal solutions, is as follows:—The liquid, diluted with a large quantity of water, is poured in a glass, and hydrosulphuret of ammonia is added, a very great excess of which should be avoided<sup>3</sup>. The whole is then covered with brown paper, and left at rest for some time in a moderately warm place. The excess of hydrosulphuret of ammonia is slowly destroyed by the oxygen and carbonic acid of the atmospheric air, whilst the sulphuret of nickel precipitated does not become oxydised. When the supernatant liquor is no longer of a brownish colour, the sulphuret of nickel is collected on a filter and washed rapidly with water to which a very small quantity of hydrosulphuret of ammonia has been added<sup>4</sup>. By

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<sup>1</sup> Dr. Fresenius says, that hydrated sulphuret of nickel is quite insoluble in hydrosulphuret of ammonia, perfectly saturated with sulphuretted hydrogen [which, however, being seldom the case, must be attended to here], but that it is soluble, to a certain extent, in hydrosulphuret of ammonia containing an excess of ammonia.—It is slightly soluble, also, in pure ammonia.—Ed.

<sup>2</sup> The sulphuret of nickel dissolved in unsaturated hydrosulphuret of ammonia or in pure ammonia, is gradually deposited by exposure to the air.—Ed.

<sup>3</sup> Although sulphuret of nickel is not oxydised by the air in the liquor in which it is precipitated, yet, according to Dr. Fresenius, when left exposed in a moist state to the atmosphere, it gradually becomes oxydised, and is slowly converted into sulphate of protoxyde of nickel.—Ed.

<sup>4</sup> Before pouring the hydrosulphuret of ammonia, the liquor, if acid, should be nearly neutralised with ammonia.—Ed.

operating with due care, the liquor filtered from the sulphuret of nickel may be obtained free from nickel. It is very seldom, if ever, that the excess of hydrosulphuret of ammonia which has been added to the nickel solution can be completely decomposed by a weak acid, for example, by acetic acid, without at the same time decomposing a little of the sulphuret of nickel which has been precipitated. No sooner is the least excess of this acid used, than the liquor filtered from the sulphuret is found to contain oxyde of nickel in solution.

\* The sulphuret of nickel obtained is treated as the corresponding sulphuret of cobalt (page 130), in order to convert it into oxyde of nickel. Like sulphuret of cobalt, that of nickel is not decomposed by muriatic acid alone.

#### \* DETERMINATION OF PEROXYDE OF NICKEL.

Peroxyde of nickel is converted into protoxyde of nickel by ignition. It may also dissolve with the help of heat in muriatic acid under disengagement of chlorine, and a solution of potash being added to this liquor precipitates oxyde of nickel from the solution.

#### SEPARATION OF OXYDE OF NICKEL FROM OXYDE OF COBALT.

Oxyde of nickel is difficultly separated from oxyde of cobalt. The most celebrated chemists have proposed more or less accurate methods for the purpose. We cannot speak here of the means which should be employed to obtain oxyde of nickel free from oxyde of cobalt, without taking care at the same time to ascertain the whole quantity of the oxyde which it might contain. I shall indicate only those which answer best for separating these two oxydes quantitatively.

The best method is that of Phillips. It consists in dissolving the two oxydes in an acid and supersaturating the solution by ammonia. If a little oxyde of cobalt is precipitated thereby, the ammoniacal salt formed was not in sufficient quantity. The liquor should therefore be rendered acid again, and it should

be supersaturated a second time by ammonia, or a sufficient quantity of sal-ammoniac may at once be added to the solution and then it may be supersaturated by ammonia, after which no precipitate will be formed. The solution is ordinarily blue, even when the proportion of the oxyde of cobalt is greater than that of the oxyde of nickel. It is then largely diluted with water. The quantity of water to be added is so much larger as the proportion of the oxyde of cobalt is more abundant; yet care must be taken that the water thus added should have been boiled long enough to expel all the atmospheric air it might contain.

The diluted solution is poured whilst still hot in a flask which can be closed; solution of pure potash is added, and the flask is corked up. The potash precipitates the oxyde of nickel only from the ammoniacal liquor, the oxyde of cobalt remaining entirely in solution. When the liquor, under the influence of the potash added, has entirely lost its blue colour, and has assumed a clear deep-red tinge, which is due to the oxyde of cobalt in solution, the operator may presume that he has poured a sufficient quantity of alkali.

As soon as the oxyde of nickel has entirely settled, the clear supernatant liquor is poured on a filter, after which the precipitate itself is thrown upon the filter and washed thereon with hot water. The dilution of the solution of the two oxydes with water free from atmospheric air is necessary because oxyde of cobalt is often converted in an ammoniacal liquor into peroxyde of cobalt, which precipitates under the form of a black powder, and mixes with the oxyde of nickel. The more diluted the solution is, the less easily can oxyde of cobalt absorb oxygen.

In such cases the quantity of potash which the operator is obliged to use is often very considerable when the liquor contains much ammonia. Wherefore, when after having added potash to the ammoniacal liquor no precipitate is obtained, a fresh quantity of this reagent must be poured in, and the operator should not be in a hurry to conclude that the solution contains no oxyde of nickel. The larger the quantity of muriate of

ammonia contained in the liquor is, the larger is also the quantity of potash required to precipitate the oxyde of nickel, and the more free it is from oxyde of cobalt.

The best manner of separating the oxyde of cobalt from the liquor filtered from the oxyde of nickel consists in precipitating it by hydrosulphuret of ammonia, and treating the sulphuret of cobalt produced as has been said (page 130).

\* If the solution contains magnesia besides oxyde of cobalt and of nickel, the separation does not take place, according to Berzelius, because the solution of potash precipitates from the ammoniacal liquor a combination of oxyde of cobalt and of magnesia, which has a green colour, like that of oxyde of nickel. Whether oxyde of cobalt remains or not in the solution depends on the quantity of magnesia contained in it.

\* Besides this method of Phillips for separating the oxydes of cobalt and of nickel, another method is frequently resorted to which was contrived by Laugier. This method, however, is applicable only when the quantity of oxyde of nickel is very small compared to that of oxyde of cobalt; but then it deserves commendation. The two oxydes are precipitated by a solution of potash and they are then treated by a solution of oxalic acid, which converts them into oxalates almost insoluble in an excess of oxalic acid, so that the supernatant liquor may be decanted, or evaporated separately, and the residuum added to the above salts, which are then to be dissolved in an excess of ammonia; the solution is diluted with water, and left at rest for a long time, at the ordinary temperature, by which means the ammonia is slowly dissipated. As it gradually volatilises, the nickel salt separates with a green colour, whilst the salt of cobalt remains in solution. The deep pink-coloured liquor is decanted in another glass, in which it is left at rest, in order to see whether a green nickel-salt will not separate. If none is deposited, it is a proof that the liquor contains none.



Let the ~~nickel salt~~ which has deposited is not free from cobalt. The best is to dissolve it in ammonia, and to resort to Phillips' method to separate the oxydes of the two metals by pouring solution of potash in the liquor.

\* The best method of separating cobalt from all the ammoniacal solutions of cobalt consists in precipitating it in the state of sulphuret by means of hydrosulphuret of ammonia<sup>1</sup>.

<sup>1</sup> Another method of separating cobalt from nickel was proposed by M. Liebig by means of cyanide of potassium. When a mixture of cyanide of potassium, and an excess of hydrocyanic acid, and of oxyde of cobalt, or of a salt of cobalt is heated, the cobalt passes into the state of cobalti-cyanide of potassium, the aqueous solution of which is not decomposed by muriatic acid, sulphuric or nitric acid, even at a boiling temperature.

The salts of nickel and oxyde of nickel are precipitated by cyanide of potassium, but the precipitate is redissolved by an excess of the reagent. This solution has a yellowish colour. The combination of cyanide of nickel and of potassium is not decomposed by acetic acid, but weak sulphuric acid decomposes it, and precipitates the cyanide of nickel.

The solution of the salt of nickel and of cobalt is accordingly rendered strongly acid by muriatic acid, and cyanide of potassium is added in sufficient excess to redissolve the precipitate which forms at first. The liquor contains then free hydrocyanic acid, cyanide of potassium, and cyanides of nickel, and of cobalt. The solution is exposed to a gentle heat, which converts the latter into cobalti-cyanide of potassium. If dilute sulphuric acid be now added in the cold to the mixture, the proportion of the protoxyde of cobalt may be to that of the nickel = 2 : 3, that is to say, in a proportion corresponding to the composition of cobalti-cyanide of nickel,  $\text{Co}_2 \text{Cy}_3, 3 \text{Ni}$ , which forms a precipitate of a bluish white colour, and the filtered liquor no longer contains cobalt or nickel. If the solution contains less nickel, the precipitate is the same as above, viz.  $\text{Co}_2 \text{Cy}_3, 3 \text{Ni}$ , but the filtrate retains a proportion of cobalti-cyanide of potassium,  $\text{Co}_2 \text{Cy}_3, 3 \text{K}$ , and also chloride of potassium  $\text{K Cl}$ . If the quantity of nickel is more considerable, the precipitate consists of cyanide of nickel and of cobalti-cyanide of nickel,  $\text{Co}_2 \text{Cy}_3, 3 \text{Ni Cy}$ , and the solution contains chloride of nickel and chloride of potassium  $\text{Ni Cl} + \text{K Cl}$ .

In the next step, when the solution containing the precipitate produced by the sulphuric acid is put in a flask, tilted obliquely to prevent spitting, and boiled until the liquor has evaporated and has disappeared. An excess of carbonate of potash, which has been previously washed, is added, and the whole is boiled for a short time. The cobalti-cyanide of nickel is thereby decomposed, and hydratal protoxyde of nickel is precipitated in white, may, in consequence, be collected on a filter, and washed with water. The solution filtered liquor contains all the cobalt in the state of cobalti-cyanide of potassium, nitric acid or nitrate of potash, is therefore subjected to a further evaporation to dryness; the residuum is then ignited, and by the weight of the residue the cobalt may be obtained.

This method is especially applicable for the analysis of the ores of cobalt in which nickel is present, but the ores of nickel which contain only small quantities

## SEPARATION OF OXYDE OF NICKEL FROM OXYDE OF ZINC.

If these two oxydes have to be separated from a solution, one of pure potash is to be added thereto, in order to dissolve the oxyde of zinc. The separation cannot be completely effected in this way because the greatest possible excess of potash could not dissolve the totality of the oxyde of zinc even by boiling the whole. The oxyde of zinc dissolves, it is true, in potash, but a very great portion of it is precipitated with the oxyde of nickel. The same thing happens when both oxydes have been dissolved in ammonia; in this case also, if potash be further added, oxyde of zinc dissolves, but the precipitated oxyde of nickel retains still a great deal of it.

Yet the separation of the two oxydes may be effected, as shown by Smith, by converting them into acetates, adding free acetic acid to the liquor, and precipitating the zinc in the state of sulphuret. The process is the same as for separating oxyde of zinc from protoxyde of manganese (page 121), and of oxyde of cobalt (page 132). The only essential point here is, that the liquor should contain no strong acid, but acetic acid only.

\* If the nickel and the zinc are in the metallic state in the

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of cobalt, the operator must carefully decompose the solution of the cyanides in cyanide of potassium, by adding a pretty considerable excess of muriatic acid, and boiling the whole for at least one hour. In that case the precipitate contains cyanide of nickel at the same time, which, reacting with the potash, becomes converted into cyanide of potassium and oxyde of nickel; the cyanide of potassium retains a little cyanide of nickel in solution. By boiling the precipitate with muriatic acid, the cyanide of nickel is decomposed, and chloride of nickel is produced, and also hydrocyanic acid, which, however, being expelled by the boiling, does not hinder the complete precipitation. Cobalti-cyanide of nickel is not attacked by boiling muriatic acid; the cobalt is not, therefore, completely redissolved. The boiling is known to have lasted long enough when the liquor no longer evolves the odour of hydrocyanic acid.

The cyanide of potassium employed generally containing a little cyanate of potash, its decomposition by the muriatic acid produces some ammonia, which remains in combination, so that on adding caustic potash after boiling, a disengagement of ammonia is produced, which retains in solution a certain quantity of oxyde of nickel, which, however, may be separated by boiling, or by adding more caustic potash.—Ed.

substance under examination, which is the case with several alloys lately in use as a substitute for silver, they should be dissolved in nitric acid or aqua regia, after which by pouring, with the requisite precautions, in the above solution, one of carbonate of alkali, the oxydes are precipitated and dissolved in an excess of acetic acid; they may then be separated by means of sulphuretted hydrogen gas.

If the combination contains other metals besides, other means are resorted to for isolating them. If copper, for example, be present, a method is adopted which will be developed farther on when treating of this metal.

\* The analyst must always bear in mind in such cases, that carbonate of alkali does not completely precipitate oxyde of nickel. (See the additional note, page 132).

#### SEPARATION OF OXYDE OF NICKEL FROM PEROXYDE OF IRON.

Peroxyde of iron is separated from oxyde of nickel by a method which is similar to that employed for isolating it from oxyde of cobalt. Ordinarily, if the solution of the two oxydes contains a sufficient quantity of muriate of ammonia, or of other ammoniacal salts, ammonia is poured into it, which precipitates the peroxyde of iron, the liquor is rapidly filtered, and the precipitate washed. The oxyde of nickel is thus precipitated from the filtered liquor by solution of potash.

A more accurate result is obtained when succinate of alkali is employed to separate peroxyde of iron from oxyde of nickel, following the method described for separating this oxyde from protoxyde of manganese (page 87), and from oxyde of cobalt (page 135).

\* The best method, however, is that of Fuchs, which consists in the use of carbonate of lime, or, better still, of baryta, because baryta is more easily separated from the unprecipitated oxyde of nickel than lime. The rules which have been traced (page 91)

for separating protoxyde of manganese and peroxyde of iron from each other, must be followed.

#### SEPARATION OF OXYDE OF NICKEL FROM PROTOXYDE OF IRON.

When protoxyde of iron has to be separated from oxyde of nickel, it should be converted into peroxyde of iron, for which purpose the combination should be heated with nitric acid.

#### SEPARATION OF OXYDE OF NICKEL FROM PROTOXYDE OF MANGANESE.

Protoxyde of manganese is very difficult to separate from oxyde of nickel, but the same method as that which has been indicated for separating protoxyde of manganese from oxyde of cobalt may be resorted to (page 137).

#### SEPARATION OF OXYDE OF NICKEL FROM ALUMINA AND GLUCINA.

These earths may be separated from oxyde of nickel by means of a solution of pure potash, by nearly the same process as that employed for separating them from oxyde of cobalt (page 140).

#### SEPARATION OF OXYDE OF NICKEL FROM MAGNESIA.

As oxyde of nickel is very difficult to separate completely in the state of sulphuret by means of hydrosulphuret of ammonia, its separation from magnesia is difficult. The best way is the following:—To the solution of the two oxydes, muriate of ammonia is added in sufficient quantity to prevent the ammonia, which is subsequently added, from producing a precipitate; the oxyde of nickel is then separated in the state of sulphuret by means of hydrosulphuret of ammonia. If the solution of the two oxydes is acid, there is no occasion to add muriate of ammonia. The operator must avoid as much possible putting a large excess of hydrosulphuret of ammonia, and the whole is left at rest in contact with the air in a moderately warm place, until the sulphuret of nickel has completely deposited. The

liquor is then filtered, the precipitate is washed with water, to which a very small quantity of hydrosulphuret of ammonia has been added. The sulphuret of nickel thus obtained is treated as we said before. The liquor filtered from it is then rendered acid by pouring an acid in it, heated, filtered again, and the magnesia is separated from it as usual.

\* Attention must here be paid to what was said when I spoke of the separation of oxyde of cobalt from magnesia. If the oxyde of nickel obtained contained still some magnesia, it might be recognised, and approximatively separated, by the means which have been indicated in reference to oxyde of cobalt.

\* If the magnesia and the oxyde of nickel can be obtained in the state of neutral acetates, the nickel may be completely separated in the state of sulphuret, by passing a current of sulphuretted hydrogen gas through the diluted solution; the magnesia remains in solution, provided always that no free acetic acid exists in the liquor.

Magnesia and oxyde of nickel cannot be separated from each other, when both are contained in an ammoniacal liquor, by adding thereto a solution of phosphate of soda which precipitates the magnesia, because the ammonia-phosphate of magnesia which is thus obtained contains oxyde of nickel, which no excess of ammonia can remove, and from which it receives a greenish tinge.

#### SEPARATION OF OXYDE OF NICKEL FROM LIME.

Oxyde of nickel may be separated from lime in the following manner:—The diluted solution of the two oxydes is rendered ammoniacal, the lime is then precipitated by oxalate of ammonia, and the liquor is rapidly filtered. Solution of pure potash being now poured in the filtered liquor, the oxyde of nickel is precipitated.

#### SEPARATION OF OXYDE OF NICKEL FROM STRONTIA AND BARYTA.

(Oxyde of nickel is separated from strontia and baryta by means of sulphuric acid, which precipitates the two earths, after

which the oxyde of nickel may be separated from the filtered liquor by means of solution of potash.

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The French edition has the following remark by M. E. Peligot :—

“ According to Messrs. Haidlen and Fresenius, oxyde of nickel may be separated from lime, baryta, and strontia, by adding to the liquor an excess of cyanide of potassium, and then carbonate of potash ; heat is applied, and the insoluble carbonates of the alkaline earths are separated by filtering from the solution of the double cyanide of nickel and of potassium. The filtered liquor is boiled for a long time with muriatic acid, until all the hydrocyanic acid is expelled, which is a sign that the decomposition of the cyanides is complete. The solution contains then chloride of nickel from which oxyde of nickel is precipitated by potash.”

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#### SEPARATION OF OXYDE OF NICKEL FROM THE ALKALIES.

\* The same process which is employed for separating oxyde of nickel from magnesia, is employed to separate it from the alkalies. This separation may often be effected by exposing these dry compounds to a current of hydrogen gas, which reduces the oxyde of nickel in the state of metallic nickel, from which the alkalies or the alkaline salts may be separated by water. This method is especially applicable when the bases exist in the state of metallic chlorides. The chlorides of the alkalisable metals are not altered by hydrogen gas, whilst chloride of nickel is reduced thereby into metallic nickel under disengagement of muriatic acid gas.

## CHAPTER XIX.

## CADMIUM.

*Carbonate of potash* is the best reagent for precipitating oxyde of cadmium from its solutions. It forms a white precipitate<sup>1</sup> which is to be dried and ignited. During the ignition carbonic acid and water are disengaged, and the oxyde remains in the form of a brown powder. As this oxyde is reduced by carbon, and is then most easily volatilised, the filter should be freed, as much as possible, of the particles which might be adhering to it, and burnt to ashes by itself.

Oxyde of cadmium is not so completely precipitated by carbonate of ammonia as by carbonate of potash.

SEPARATION OF OXYDE OF CADMIUM FROM THE OXYDES OF  
NICKEL, OF COBALT, OF ZINC, OF IRON, AND OF MANGANESE,  
FROM THE EARTHS AND FROM THE ALKALIES.

Oxyde of cadmium may be separated from the oxydes hitherto treated of by simply acidifying the solution by the addition of an acid, for example, by muriatic acid, diluting it with a large quantity of water, and slowly passing a current of sulphuretted hydrogen gas through the diluted liquor to complete saturation, and therefore until it smells strongly of the gas, even after the disengagement of the gas has ceased to be passed through it. Sulphuret of cadmium is precipitated thereby, which is insoluble

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<sup>1</sup> This white precipitate is carbonate of cadmium.—ED.

in a dilute acid solution, whilst the oxydes of nickel, of cobalt, of zinc, of iron, and of manganese are not precipitated from their acid solutions, even when dilute, by sulphuretted hydrogen.

When oxyde of zinc has to be separated from oxyde of cadmium by this process, it is necessary to add to this solution a larger proportion of acid than is necessary to isolate the latter from the oxydes of nickel, of cobalt, of iron and of manganese.

Sulphuretted hydrogen does not alter the solutions of the earths and of the alkalies, and therefore it is an excellent reagent for easily separating oxyde of cadmium from these substances.

The colour of the sulphuret of cadmium produced varies according to the state of dilution of the solution from which it is precipitated. It is orange yellow, or yellow. This precipitate may be collected upon a weighed filter and washed with pure water. It is then carefully exposed to a very moderate heat, until after several successive weighings it is seen to lose no more weight, and from the weight the quantity of the oxyde of cadmium, or of the cadmium, is calculated.

Yet in such a method of analysis it is necessary that the operator should be thoroughly convinced that no excess of sulphur has fallen down with the sulphuret of cadmium, because, should this have taken place, the weight of the sulphuret would be thus more or less augmented. The sulphuret of cadmium may be contaminated by sulphur when, after having effected its precipitation by means of sulphuretted hydrogen, the solution remains exposed for a long time to the air; in such a case the sulphuretted hydrogen dissolved in the water deposits sulphur. The same effect is produced also when the acid liquor from which the sulphuret of cadmium is intended to be precipitated contains peroxyde of iron; the latter is reduced by sulphuretted hydrogen to the state of protoxyde of iron, which remains in solution, and the liberated sulphur is precipitated with the sulphuret of cadmium.

It is therefore a good precaution to redissolve the precipitated sulphuret of cadmium, and to reprecipitate it in the state of oxyde of cadmium by pouring carbonate of potash in the solution.



The filter with the sulphuret, whilst still moist, is removed from the funnel and put in a glass, concentrated muriatic acid is then poured upon it, and the whole is digested at a gentle heat, until all odour of sulphuretted hydrogen has vanished; the liquor is filtered, and oxyde of cadmium is precipitated therefrom as above said.

When oxyde of cadmium has been thus separated from the other substances, these may be isolated from the solution filtered from the sulphuret of cadmium. Before, however, proceeding to do this, the liquor must be very gently heated until all odour of sulphuretted hydrogen has disappeared. If it contained peroxyde of iron, it will have been converted, as we said, into protoxyde of iron, wherefore it should be reconverted into peroxyde of iron by means of nitric acid or of chlorine gas.

Oxyde of cadmium may likewise be completely precipitated from a neutral or ammoniacal solution by hydrosulphuret of ammonia, but in such a case, it is necessary to treat the precipitate which will have formed, by muriatic acid, and to reprecipitate oxyde of cadmium from its solution by means of carbonate of potash.

## CHAPTER XX.

## LEAD.

## DETERMINATION OF LEAD AND OF PROTOXYDE OF LEAD.

*Oxalate of ammonia* is the best reagent for precipitating protoxyde of lead from its solutions. As for lime, it is necessary that the liquor should be neutral, or very feebly ammoniacal. After having washed and dried the oxalate of lead produced, it is ignited in a small counterpoised porcelain crucible, which must be left uncovered. It is thereby converted into protoxyde of lead, from the weight of which the quantity of lead, if it existed in the metallic state in the compound, may be calculated <sup>1</sup>.

If, as is generally done with the other precipitates, the filter containing the oxalate of lead were burnt, the charcoal of the paper might reduce a little oxyde of lead.<sup>2</sup> The oxalate of lead should therefore be detached from the filter as much as possible, and the filter burnt to ashes by itself. Before weighing, the ashes should be added to the calcined precipitate. The best is to burn the filter in the platinum crucible before igniting the oxalate. The same precaution must be adopted for calcining the other precipitates of lead, except sulphate of lead. The operation should always be performed, when practicable, in small and very thin porcelain crucibles, upon an argand spirit-lamp.

<sup>1</sup> The liquor must be neutral, or slightly ammoniacal, because some oxalate of lead might otherwise be redissolved. Strictly speaking, oxalate of lead is not, according to Dr. Fresenius, altogether insoluble in water, and if ammoniacal salts are present, its solubility is augmented.—Ed.

<sup>2</sup> In which case the platinum crucible would unavoidably be perforated.—Ed.

Oxyde of lead may also be precipitated by means of *carbonate of ammonia*, but in that case the liquor should be heated. If the carbonate of ammonia employed contains much bicarbonate, it is advisable to add a little pure ammonia, because without this precaution the oxyde of lead would not be completely precipitated, traces of which would remain in the solution; these traces are, however, very trifling. The carbonate of lead thus obtained is ignited in a porcelain crucible, just as the oxalate of lead above, by which the carbonic acid is expelled, and it is converted into protoxyde of lead, the weight of which is determined.

If protoxyde of lead has to be determined in the state of sulphate, it is necessary, after having added *sulphuric acid* to the solution<sup>1</sup>, to evaporate it to dryness, and to heat the residuum in a platinum crucible, until all the excess of sulphuric acid has volatilised. The sulphate of lead left behind is then weighed. The calcining just mentioned may take place in a platinum crucible, provided the sulphate operated upon contains no organic substances.

When a combination contains lead in the metallic state, it should be dissolved in nitric acid. The solution then contains protoxyde of lead, the quantity of which may be determined by one of the methods just mentioned, and from which that of the lead may be easily calculated.

\* Determination of the peroxydes of lead [*suroxyde plumbeux* (red lead)  $2\text{PbO} + \text{PbO}_2$  and *suroxyde plombique*—*binoxyde* or *puce oxyde* of lead  $\text{PbO}_2$ ]. These oxydes may be converted into protoxyde of lead by ignition. If contained, however, in substances which must not be calcined, they may be converted into chloride of lead by heating them for a long time in muriatic acid, in which case there is a disengagement of gaseous chlorine.

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<sup>1</sup> The sulphuric acid employed should be moderately dilute and in excess, and the precipitated sulphate of lead should be washed with aqueous alcohol, or, if alcohol is objectionable, with water acidified with sulphuric acid, dried, and then ignited, but not with the filter, for the charcoal would reduce part of the sulphate. If a platinum crucible is used, the ignition must be cautiously performed, for fear of reducing some lead and damaging the crucible. A thin porcelain crucible may be used.—ED.

The chloride of lead obtained may then be dissolved by means of a very large quantity of water, provided circumstances be such as to permit the employment of this method for separating the lead from other substances.

SEPARATION OF PROTOXYDE OF LEAD FROM OXYDE OF CADMIUM.

\* The best mode of separating protoxyde of lead and oxyde of cadmium from each other, consists in pouring sulphuric acid in the solution of these two oxydes, evaporating the liquor to dryness, and moderately heating the residuum, until the excess of sulphuric acid employed has dissipated. The dry mass is then treated by water, which dissolves the sulphate of cadmium, whilst the sulphate of lead remains insoluble. The latter should be washed with only a small quantity of water, because it is not quite insoluble in that menstruum, after which it is ignited and weighed. Before igniting it, the filter is burnt upon the cover of the crucible; carbonate of potash being then poured in the solution of the sulphate of cadmium precipitates oxyde of cadmium therefrom.

\* This method, however, cannot give a very accurate result, because sulphate of lead is not perfectly insoluble in water.

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The following observation has been added by Ed. Peligot in the French edition :—

\* “Messrs. Haidlen and Fresenius separate these two oxydes by adding to their solution an excess of one of cyanide of potassium, by heating, the whole of the lead separates, and all the cadmium remains in solution in the state of double cyanide of cadmium and of potassium. The cadmium may now be separated by sulphuretted hydrogen, or else this solution may be boiled with muriatic acid until the whole of the hydrocyanic acid has been expelled, after which the precipitation is effected by means of carbonate of potash. As the precipitated lead always contains some potash, it should be redissolved in nitric acid, from which the oxyde of lead is precipitated by oxalate or carbonate of ammonia.”—E. P.

SEPARATION OF PROTOXYDE OF LEAD FROM THE OXYDES OF  
NICKEL, OF COBALT, OF ZINC, OF IRON, OF MANGANESE,  
FROM THE EARTHS AND THE ALKALIES.

As protoxyde of lead is precipitated by a current of sulphuretted hydrogen from a dilute acid solution, this method is better than any which might be resorted to for separating it from the substances hitherto treated of, since they, except oxyde of cadmium, are not precipitable from their acid solutions by sulphuretted hydrogen. The best in such a case, if the solution of the oxydes is neutral, is to acidify it by means of nitric acid, and not by hydrochloric acid, because the latter acid might produce a precipitate in a solution of oxyde of lead, if it were not diluted with a very large proportion of water. The solution rendered acid is to be diluted with water, and a current of sulphuretted hydrogen is slowly passed through it to complete saturation.

At the beginning, and when only a few bubbles of gas are as yet passing through the liquor, the precipitate formed may appear of a reddish brown colour, if the liquor contains muriatic acid, or when peroxyde of iron is present, but when the disengagement has become more copious, and provided the quantity of protoxyde of lead contained in the solution is not too feeble compared to that of the peroxyde of iron, the precipitate becomes black.

The sulphuret of lead which has precipitated might be collected and washed with pure water, and then carefully dried at a very gentle heat, until the weight should remain constant; and then from its weight that of the protoxyde of lead might be calculated. But when sulphur has fallen down simultaneously with the sulphuret of lead, a circumstance which always takes place when, for example, the solution contains peroxyde of iron, it is advisable to convert the sulphuret of lead which has been obtained into sulphate of lead.

To effect this, the precipitate should be well dried, put in a glass, or in a large platinum capsula with the filter, which

should be as small as possible; then, concentrated and fuming nitric acid is gradually and with much caution poured on it. The acid must be added only in very small portions at a time, in order to avoid too violent an action, which might give rise to a projection of the mass. It is also necessary to take care to cover the glass or capsula with a plate of glass. In this manner the sulphuret of lead is completely converted into sulphate of lead. If fuming nitric acid were not employed, sulphur would separate, which it would be found difficult to oxydise even by a prolonged digestion. When the action of the nitric acid upon the sulphuret of lead has ceased, a drop or two of sulphuric acid may be added to the oxydised mass; after which the sulphate of lead produced is moderately heated until no acid vapours are any longer disengaged; after which it is ignited, which destroys the organic matter of the filter, which burns in the air without reducing the sulphate of lead, which, after ignition, is weighed.

\* The sulphuret of lead obtained may also be treated by concentrated muriatic acid, which produces a disengagement of sulphuretted hydrogen. Nitric acid is next added, and the whole is evaporated to dryness; the filter is thus completely oxydised. The dry mass is put in a porcelain crucible, sulphuric acid is poured upon it with care, and heat is applied until the excess of sulphuric acid, which may have been employed, has volatilised; after which the sulphate of lead produced is weighed. It is not advisable to weigh in that state the chloride of lead obtained from the sulphuret of lead.

As to the liquor filtered from the sulphuret of lead, it should be heated until all odour of sulphuretted hydrogen has disappeared; after which the other substances may then be separated. If peroxyde of iron existed with protoxyde of lead in the original solution, it will have been converted by sulphuretted hydrogen into protoxyde of iron; wherefore, the liquor should be treated by nitric acid, or by chlorine gas.

This method of separating protoxyde of lead by sulphuretted hydrogen, from other oxydes which are not capable of being precipitated from their acid solutions by this reagent, deserves

to be preferred to all the other processes which might be employed, for example, to that which consists in precipitating protoxyde of lead by means of sulphuric acid, when the other base combined with it forms with sulphuric acid salts which are soluble.

Protoxyde of lead may also be precipitated in the state of sulphuret of lead by means of hydrosulphuret of ammonia from solutions which are neutral or ammoniacal, especially for separating it from some earths or from the alkalies. Yet the sulphuret of lead obtained must be converted into sulphate of lead. If the hydrosulphuret of ammonia employed contains an excess of sulphur, the precipitate of sulphuret of lead produced has a reddish-brown colour, but in a short time this precipitate turns black.

\* Protoxyde of lead may be separated from most of the oxydes mentioned, not only by sulphuretted hydrogen, but also by the method which consists in reducing them into metallic chlorides by means of muriatic acid, and strong alcohol being used for separating the chloride of lead from the other metallic chlorides, and which are nearly all soluble in this menstruum.<sup>1</sup> In many cases the precipitation cannot be effected by the ordinary reagents, because the action of alcohol upon metallic chlorides produces organic combinations, which will prevent a portion of the oxydes of these metals from being precipitated by the alkalies, but by means of sulphuretted hydrogen gas or of hydrosulphuret of ammonia, they may be completely separated in the state of sulphurets.

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<sup>1</sup> The alcohol is next expelled from the liquor by heat; the residuum is then dissolved in water, and the oxydes are then precipitated from this solution.—Ed.

## CHAPTER XXI.

## BISMUTH.

## DETERMINATION OF BISMUTH AND OXYDE OF BISMUTH.

\* THE best reagent for precipitating oxyde of bismuth from its solution is *carbonate of ammonia*, by an excess of which this oxyde is completely precipitated. Whether the solution which contains the bismuth is clear, diluted, or acid, or whether it has become milky by the water which has been added, is of no consequence. At the beginning, carbonate of ammonia dissolves a very large quantity of oxyde of bismuth, but after leaving the whole at rest for a few hours in a warm place, the oxyde of bismuth is completely separated, and the liquor filtered from it retains only imponderable traces of it.<sup>1</sup>

The precipitate is very easily washed. When dry, it is ignited in a porcelain crucible, which deprives it of its white colour and renders it yellow: when the heat of the spirit-lamp is not too strong it does not fuse.<sup>2</sup> The precipitate is scraped from the filter as well as possible and the filter is then burnt to ashes by itself.

*Carbonate of potash* and pure *potash* precipitate oxyde of bismuth as completely as carbonate of ammonia, yet the preci-

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<sup>1</sup> It is better, after having added the carbonate of ammonia, to heat the whole for a little time, otherwise the filtrate may hold a more or less considerable portion of basic carbonate of bismuth in solution, which would render the analysis quite incorrect.—Ed.

<sup>2</sup> When, however, the heat has been strong enough to fuse it, its weight, notwithstanding, remains the same; but it must not be ignited with the filter, the charcoal of which would reduce the oxyde of bismuth.—Ed.



pitrate always contains traces of potash however carefully it may have been washed ; but carbonate of soda does not precipitate oxyde of bismuth so completely as carbonate of ammonia and carbonate of potash.

\* When carbonate of ammonia is employed to precipitate oxyde of bismuth quantitatively, it is absolutely necessary that the solution be completely free from muriatic acid.<sup>1</sup> If this is not the case, the oxyde of bismuth is totally precipitated, it is true, but the precipitate is then mixed with chloride of bismuth, which cannot be completely decomposed by any excess whatever of the reagent, even though carbonate of potash be employed. When, after drying it, this precipitate is ignited, chloride of bismuth volatilises, and the oxyde of bismuth remains behind, which, however, retains still some chloride of bismuth.

Wherefore, in quantitative analysis, oxyde of bismuth should always be dissolved in nitric acid, and not in aqua regia.

If oxyde of bismuth has to be quantitatively determined in a solution which contains muriatic acid, it should be precipitated as *sulphuret of bismuth*, which may be done by simply adding hydrosulphuret of ammonia ; sulphuret of bismuth is thus precipitated ;—it must be well washed, removed when still moist from the funnel along with the filter, and nitric acid is poured upon it. Sulphuret of bismuth is attacked by this acid even in the cold, yet a moderate heat is applied until the liberated sulphur has assumed a pure yellow colour, but the digestion must not be prolonged too much. The liquor is then filtered, the sulphur is washed with water acidulated with nitric acid, and the oxyde of bismuth is precipitated therefrom by carbonate of ammonia.

When a compound contains metallic bismuth, it is dissolved by nitric acid ; the quantity of the oxyde of bismuth in the solution is then determined as above said, and that of the metal is calculated accordingly.

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<sup>1</sup> In fact no other mineral acid, except nitric acid, should be present, for in such solutions carbonate of ammonia would precipitate a mixture of basic carbonate of bismuth, and of another basic salt of the same metal with the other acid.—ED.

## SEPARATION OF OXYDE OF BISMUTH FROM PROTOXYDE OF LEAD.

\* Although protoxyde of lead and its combinations are completely soluble in a solution of hydrate of potash, and oxyde of bismuth is insoluble therein, this reagent cannot be resorted to for separating these two oxydes from each other. The oxyde of bismuth which remains undissolved contains a considerable quantity of oxyde of lead which cannot be dissolved even by boiling it again with a fresh solution of potash.

Oxyde of bismuth being completely precipitated by carbonate of ammonia when this reagent is added in excess, and the whole left at rest for some time, the method proposed by Laugier, and which consists in dissolving the oxyde of bismuth in an excess of carbonate of ammonia, and filtering the liquor from the carbonate of lead left in an insoluble state, cannot yield accurate results.

\* According to Sander, *carbonate of baryta* cannot serve to separate oxyde of bismuth and of lead from each other.

The separation of these two oxydes may be effected as follows:—An excess of sulphuric acid is added to the solution of the two oxydes, and the liquor is evaporated until the excess of the sulphuric acid begins to volatilise. Water is then added, which dissolves the sulphate of bismuth, and produces a perfectly clear liquor if a sufficient quantity of sulphuric acid still predominates. The sulphate of lead remains insoluble. It is collected on a filter, and washed with water acidulated with a little sulphuric acid; it is then dried and ignited. The oxyde of bismuth is precipitated from the filtered liquor by carbonate of ammonia.

It is necessary to add sulphuric acid to the somewhat diluted solution of the two oxydes, if the liquor contains too little of the acid, and to filter rapidly, otherwise some sulphate of bismuth in small crystals is also deposited.

This method, however, does not afford very accurate results, because sulphate of lead is not perfectly insoluble in water, nor

in solution; yet sulphuric acid dissolves it much less than the other acids.\*

\* *Another method* for separating these two metals or their oxydes from each other, is the following:—The two metals or their oxydes are dissolved in nitric acid, diluted with as little water as possible. Water should not be altogether omitted, because these metals or oxydes are not completely dissolved by the concentrated acid. Muriatic acid is added to the nitric acid solution in sufficient quantity to convert the whole of the oxydes into chlorides, and still leave an excess of acid. A large quantity of strong alcohol is now poured in, to which a little ether may be added; the chloride of lead formed remains insoluble, whilst the chloride of bismuth dissolves. Chloride of bismuth is not partially decomposed by alcohol, as is the case with water. The chloride of lead is allowed to settle well; it is collected upon a counterpoised filter, and washed with alcohol containing ether. To the alcoholic solution of the chloride of bismuth, water is now added, the alcohol is volatilised at a gentle heat, and the bismuth is precipitated in the state of sulphuret by means of sulphuretted hydrogen gas.

\* This separation is so much the more successful, as the alcohol employed is stronger, and that it contains, besides the ether, a small proportion of free muriatic acid, owing to which the chloride of lead is rendered more insoluble still. Yet, in spite of all these precautions, a little less chloride of lead, amounting sometimes to as much as five per cent., is obtained, according to Sander, than should be the case, although this salt by itself is absolutely insoluble in alcohol.

\* Bismuth and lead should not be separated in the state of nitrates by means of alcohol, because nitrate of lead is not absolutely insoluble in even the strongest alcohol.

\* For the purpose of separating bismuth and lead from each

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\* According to the Pharmacopoeia, sulphuric acid dissolves in 22816 parts of pure bismuth, and in 1000 parts of lead. It is more readily dissolved with sulphuric acid.—Ed.

dissolves oxyde of cadmium without attacking oxyde of bismuth, might be employed.

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In the French edition, this note by E. Peligot:—

\* “Mr. Persoz separates these two oxydes by dissolving them both in an acid, and adding paraphosphoric acid and an excess of ammonia to the solution. Paraphosphate of bismuth is insoluble in ammonia, and may be separated by filtering.”

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SEPARATION OF OXYDE OF BISMUTH FROM THE OXYDES OF  
NICKEL, OF COBALT, OF ZINC, OF IRON, OF MANGANESE,  
FROM THE EARTHS AND FROM THE ALKALIES.

Oxyde of bismuth can be separated, by means of sulphuretted hydrogen, from all the oxydes which cannot be precipitated from an acid solution by this reagent. Yet when the precipitation of sulphuret of bismuth is intended to be made by means of sulphuretted hydrogen, it is necessary to take care to dilute with water the solution of the oxyde of bismuth. But as the solutions of bismuth are rendered milky by water, acetic acid should first be added to the liquor, which prevents its becoming turbid when water comes to be poured into it. This addition being made, a current of sulphuretted hydrogen is passed through the liquid. As to the sulphuret of bismuth which falls down, it is decomposed in the manner described before, after which the oxyde is precipitated from the nitric acid solution by means of carbonate of ammonia.

Oxyde of bismuth is thus separated, by the above method, from the oxydes of nickel, of cobalt, of zinc, of iron, and of manganese, and also from the earths and the alkalies. The substances with which it was combined are subsequently separated from the liquor filtered from the sulphuret of bismuth. Yet when these substances are not such as can be precipitated by carbonate of ammonia, as is the case with the fixed alkalies, sulphuretted hydrogen need not be employed at all, and the solution of carbonate of ammonia alone is sufficient to separate them from the oxyde of bismuth.

## CHAPTER XXII.

## URANIUM.

## DETERMINATION OF PEROXYDE OF URANIUM.

**PEROXYDE** of uranium is completely precipitated from its solutions by ammonia. The precipitate is yellow, and besides peroxyde of uranium, it contains ammonia and water. It should not be washed with pure water, because it gradually passes with it through the filter, and thus forms a yellowish milky solution. This difficulty can only be obviated by washing it with a dilute solution of muriate of ammonia. Yet even this does not altogether prevent it. The precipitate, after washing, is dried and ignited. Ignition converts it entirely into protoxyde of uranium, and it loses, at the same time, water, ammonia, and oxygen. From the weight of the protoxyde of uranium obtained, that of the peroxyde is calculated.

When a solution from which peroxyde of uranium has to be precipitated contains a considerable quantity of an earth of whatever kind, ammonia, according to Arfvedson, precipitates, along with the peroxyde of uranium, a large proportion of the earth, even when this earth, such as, for example, baryta or lime, are not capable of being precipitated from other solutions by ammonia. Thus, when combined with an earth, peroxyde of uranium is not converted into protoxyde of uranium by ignition. Consequently, before submitting the precipitate to the action of the fire, it should be dissolved in muriatic acid, and the solution precipitated by ammonia; the precipitate is

then washed with a solution of muriate of ammonia, dried and ignited, by which means it is converted into protoxyde of uranium, which is weighed.

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\* M. E. Peligot has added the following remarks to the French edition :—

“ This method is evidently insufficient. I have lately shown that under the name of protoxyde of uranium, two distinct oxydes had been confounded ; I have called one of them deutoxyde of uranium, which is obtained by exposing to a high temperature the proto and persalts of uranium, the acid of which is volatile or decomposable by heat ; it is black, its composition is represented by  $U_4 O_3$ , U being equal to 750.

“ The other oxyde results from the peroxydisation of the protoxyde, or of the black oxyde of uranium, when these two oxydes are exposed to the action of oxygen or of the air at a dark red heat ; it has an olive green colour, its formula is represented by  $U_3 O_4$ . When strongly calcined, it is converted into black oxyde. Lastly, neither of these two oxydes enters into the composition of the green salts of uranium, as was believed to be the case by confounding the one with the other. They do not combine with acids, but are decomposed by them ; the result being a mixture of the green salt of protoxyde, and of the yellow salts of peroxyde of uranium ; for they should be considered as being both the result of the combination of the protoxyde and peroxyde of uranium united in different proportions. The green salts contain the protoxyde of uranium, which had hitherto been mistaken for the metal.

“ The properties of the two oxydes, the black and the olive, render it very difficult to dose uranium in an exact manner. When peroxyde of uranium has been precipitated from the yellow salts by ammonia, and the precipitate is ignited in a platinum crucible, black oxyde remains, if the calcining has been effected at a very high temperature ; if it has been effected at a dark red heat, and in contact with the air, the olive oxyde is obtained. More often, however, it consists of a mixture of

the two, for whilst the crucible is cooling, the black oxyde is partially transformed into the olive one; this peroxydisement is avoided as much as possible, by placing the crucible which contains the black oxyde, whilst yet very hot, upon a metallic support, for, by thus cooling it rapidly, the olive oxyde formed is in very trifling proportion, which may be neglected, since even when the peroxydisement is complete, the increase of weight from the oxygen absorbed in passing to the state of olive oxyde, does not amount to one per cent.

“ Uranium may also be dosed in the state of olive oxyde by maintaining the black oxyde in a state of great division at a dark red heat, in contact with the air. I am inclined to think, that as the formation of this oxyde takes place at a temperature which is very near that at which it is destroyed, it is pretty difficult to appreciate the time necessary to complete the peroxydisation. At any rate, a greater precision may be obtained by bringing these oxydes, or their mixture, in the state of protoxyde of uranium by means of hydrogen gas. This process is, however, of difficult execution, on account of the weighing of the latter oxyde, which is pyrophoric, and which must be performed in an atmosphere of hydrogen gas, by closing with the blowpipe the tube in which it has been produced; in calculating it therefore, the difference of the weight of the tube first weighed full of air and then filled with hydrogen, must be taken account of, neglecting, however, the gas which, owing to its extremely divided state, must have been condensed by the protoxyde of uranium.

“ These difficulties, however, exist only when the object in view is to dose uranium with an extreme degree of precision.”

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#### DETERMINATION OF PROTOXYDE OF URANIUM.

\* When a solution contains protoxyde of uranium, ammonia produces therein a precipitate of brown flakes, with a slight tinge of purple, and which are hydrate of protoxyde of uranium. In drying this precipitate it frequently happens, according to Arfvedson, that part of this hydrate oxydises and becomes yellow.

If the precipitation has been effected by a large excess of ammonia, or if it be washed with hot water, it becomes entirely converted, pending the drying, into peroxyde of uranium, containing ammonia, but which is reduced by ignition into the state of protoxyde of uranium.

\* Yet it is better to pour nitric acid in a solution which contains oxyde of uranium, and to heat the whole in order to convert the latter into peroxyde of uranium, which may then be precipitated by ammonia.

SEPARATION OF THE OXYDES OF URANIUM FROM THE OXYDES OF  
BISMUTH, OF LEAD, AND OF CADMIUM.

The oxydes of uranium are separated from the oxydes of bismuth, of lead, and of cadmium, by passing through their acidified solution a current of sulphuretted hydrogen, by which the latter oxydes are precipitated in the state of metallic sulphurets; the oxydes of uranium, on the contrary, remain in solution. The sulphuretted hydrogen is then to be expelled from the filtered liquor by heating for a long time, after which they are precipitated therefrom by ammonia.

SEPARATION OF THE OXYDES OF URANIUM FROM THE OXYDES OF  
NICKEL, OF COBALT, AND OF ZINC.

It is extremely difficult to separate the oxydes of uranium from those of the metals hitherto treated of. They may be separated from the oxydes of nickel, of cobalt, and of zinc, in the following manner :—

\* If the combination contains protoxyde of uranium, it should be converted into peroxyde of uranium by means of nitric acid, then to the diluted solution, which should not be too acid, an excess of *carbonate of baryta* is added, and the whole is left at rest for at least three days at the ordinary temperature, and stirring it frequently. The peroxyde of uranium precipitates whilst the other oxydes remain in solution. The peroxyde of uranium, with the excess of carbonate of baryta, is then dissolved



in muriatic acid, the baryta is precipitated by sulphuric acid, and the peroxyde of uranium by ammonia. The oxydes which have remained in solution are precipitated by the methods prescribed before, after having, of course, previously eliminated the baryta from the filtered solution by means of sulphuric acid.

It is absolutely necessary to leave the peroxyde of uranium and the carbonate of baryta in contact for several days, because otherwise, according to Sander, a considerable quantity of this oxyde would escape precipitation.

\* [The following process was discovered by Mr. Ebelmen for separating uranium in a complete manner from the oxydes of zinc, of cobalt, and of manganese. Uranate of potash is insoluble in carbonate of potash, but very soluble in a liquor containing bicarbonate of potash, so that when to the diluted solution of the three oxydes a slight excess of bicarbonate of potash is added, the whole of the uranium is dissolved and imparts a yellow colour to it; a soluble double carbonate of oxyde of uranium and of potash is formed, whilst the carbonates of zinc, of cobalt, and of nickel are precipitated. The operator may, therefore, according to circumstances,—first, precipitate the solution by potash and digest the precipitate thus formed with bicarbonate of potash, which will dissolve the oxyde of uranium only; secondly, precipitate the liquor by bicarbonate of potash, employed in slight excess, filter, and wash the filter so long as the liquor passes through with a yellow colour.

\* The presence of phosphoric acid in the liquid which contains the oxyde of uranium does not prevent the latter from being dissolved by an excess of bicarbonate of potash, but a greater proportion of the reagent must then be employed, unless a suitable proportion of peroxyde of iron be present, which retains all the phosphoric acid in the precipitate. By adding to a solution of phosphate and of arseniate of uranium in an excess of bicarbonate of potash, a known quantity of peroxyde of iron in solution in nitric acid, these two oxydes, according to Mr. Ebelmen, may be completely separated from the oxyde of

uranium, and the proportion is then determined by the augmentation of the weight of the peroxyde of iron, as was indicated by M. Berthier. Oxyde of uranium may also be separated by means of potash and the phosphoric and arsenic acids be left in the liquor.

\* In order to separate the oxyde of uranium from the solution, caustic potash is to be poured therein ; the whole of the oxyde of uranium falls down in the state of uranate of potash. The liquor is decanted, the precipitate is washed by decantation, by which means the greatest portion of the alkali is eliminated. The deposit must then be dissolved in muriatic acid and precipitated by ammonia. It is advisable to repeat this operation several times ; this may be done altogether without loss by using the same filter in order to eliminate the potash completely. —Ed. P.]

#### SEPARATION OF THE OXYDES OF URANIUM FROM THOSE OF IRON.

The oxydes of uranium may be separated from those of iron in the following manner:—If the oxydes of both metals are contained in a solution, an excess of carbonate of ammonia is added thereto, which dissolves the oxyde of uranium, whilst the peroxyde of iron falls down. If the oxyde of uranium and of iron exist in the state of protoxyde, they must be converted into peroxyde by heating the liquor with nitric acid.

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M. Peligot has added the following remark in the French edition :—

\* “ It is necessary to operate upon liquids very much diluted with water, and this is the case whenever carbonate of ammonia is resorted to for precipitating iron ; in effect, according to M. Wöhler, recently precipitated peroxyde of iron is entirely soluble in a large excess of carbonate of ammonia ; this salt may, nevertheless, be employed in this operation, for M. Berzelius has remarked that whatever may be the excess of this reagent employed to dissolve the hydrate of peroxyde of iron,

the latter is entirely precipitated from its solution by diluting it with a sufficient quantity of water."

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\* M. Berthier boils the solution of these metals after having added sulphite of ammonia thereto. The whole of the uranium precipitates in the state of basic sulphite in grains of a fine yellow colour. The iron, but only the iron, may also be separated by precipitating the two metals by means of an alkaline carbonate, treating the precipitate by sulphurous acid, and boiling; all the iron will then remain in the liquor. If the uranium contained only very small quantities of manganese of cobalt, of nickel, and of zinc, these metals would also be separated, and remain in solution.—E. PELIGOT.

#### SEPARATION OF THE OXYDES OF URANIUM FROM PROTOXYDE OF MANGANESE AND OF MAGNESIA.

In order to separate oxyde of uranium from protoxyde of manganese and from magnesia, the same process is employed as for separating their oxydes from those of cobalt, of nickel, and of zinc. Hydrosulphuret of ammonia is not suitable for separating peroxyde of uranium from magnesia, because sulphuret of uranium is not completely insoluble in an excess of this reagent.

#### SEPARATION OF THE OXYDES OF URANIUM FROM ALUMINA.

Alumina may be separated from peroxyde of uranium in the same manner as for separating it from peroxyde of iron.

#### SEPARATION OF THE OXYDES OF URANIUM FROM LIME AND STRONTIA.

Lime and strontia may be separated from peroxyde of uranium as follows:—Sulphuric acid is poured in the solution, and alcohol is added thereto; sulphate of lime and sulphate of strontia are thus precipitated, which are to be washed with alcohol. The

sulphate of peroxyde of uranium remains dissolved in the alcohol, provided a sufficient quantity of this menstruum has been employed. The alcohol being then evaporated, the peroxyde of uranium is precipitated by ammonia.

SEPARATION OF THE OXYDES OF URANIUM FROM BARYTA.

Peroxyde of uranium is separated from baryta by means of sulphuric acid, which precipitates the earth.

SEPARATION OF THE OXYDES OF URANIUM FROM THE ALKALIES.

Peroxyde of uranium may be separated from the fixed alkalies by ammonia, an excess of which must be poured in the solution; the precipitate which is thus formed is washed with a solution of muriate of ammonia. The fixed alkali may afterwards be separated from the filtered liquor.

## CHAPTER XXIII.

## COPPER.

## DETERMINATION OF COPPER AND OF PROTOXYDE OF COPPER.

THE best reagent for precipitating protoxyde of copper from its solutions, is solution of pure *potash*. The liquor which contains the protoxyde of copper is put in a porcelain capsula, or better still, in one of platinum. The whole is then moderately boiled, and a solution of potash is then added,<sup>1</sup> which separates the protoxyde of copper under the form of a heavy brownish-black precipitate.<sup>2</sup>

If the precipitation of the protoxyde of copper is performed in the cold, the precipitate is a hydrate of protoxyde of copper, which is bulky and blue, but which, however, upon being boiled, becomes heavy and brownish-black, and converted into protoxyde of copper. It is always necessary to convert the hydrate of protoxyde of copper into protoxyde of copper by heat, because the former cannot be washed so easily as the latter.

Protoxyde of copper is difficult to wash, but it may be done

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<sup>1</sup> The solution of potash must of course be added, so long as it produces a precipitate.—ED.

<sup>2</sup> The liquor which contains the salt of copper should be moderately diluted and boiled, after the addition of solution of potash before filtering, for if the solution be too concentrated, some hydrated blue oxyde may remain suspended in the liquor, and boiling will not precipitate it; on the other hand, if the solution, though dilute, is treated in the cold with solution of potash, the precipitate is blue and bulky, and is generally mixed with some of the alkali, which cannot be completely removed by washing, or, at least, without extreme difficulty.—ED.

in a complete manner; the best is to employ hot water,<sup>1</sup> because the least traces of potash may thus be eliminated. After drying, the precipitate is ignited, which may be most conveniently done in a platinum crucible, into which the filter may also be burnt. If a small portion of the protoxyde of copper was thus converted into suboxyde of copper, the latter would soon reabsorb oxygen under the influence of a current of air which may be determined into the crucible pending the ignition. The operator must take care to weigh the protoxyde of copper immediately after cooling,<sup>2</sup> in the crucible of platinum, which must be well closed, because without this precaution it attracts moisture.

The more diluted the solution of the protoxyde of copper is, the more completely is the latter precipitated by potash. If the solution be very concentrated, the liquor, after precipitation by potash, retains still traces of protoxyde of copper, and upon addition of hydrosulphuret of ammonia it turns brown, which does not take place when before adding the potash the operator has taken care to dilute it with a large quantity of water.

\* Sometimes the solution of potash fails in precipitating in the state of protoxyde of copper the whole of the copper contained in the solution. Small quantities remain dissolved, owing to which the filtered liquor turns brown when treated by hydro-sulphuret of ammonia.

\* When the solution of protoxyde of copper has been boiled for a long time with that of potash, a small quantity of protoxyde of copper is found deposited on the sides of the porcelain or platinum capsula, where it adheres so strongly, that it cannot be detached therefrom by any mechanical means. This small quantity of oxyde should then be dissolved in a few drops of dilute sulphuric acid; water is then added, and also solution of potash, and on boiling, the protoxyde of copper is precipitated. If the solution of protoxyde of copper is very dilute,

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<sup>1</sup> See my filtering apparatus, page 38.—Ed.

<sup>2</sup> The crucible must be well closed, and deposited in a metallic capsula, in order to cool it as rapidly as possible, or else it may be placed under a glass bell by the side of a dish of concentrated sulphuric acid, and rapidly weighed when cold or nearly cold.—Ed.

no particle of oxyde adheres to the sides of the vessel during the precipitation.

\* When a liquor contains protoxyde of copper dissolved in an excess of ammonia, this oxyde can be completely precipitated therefrom by ebullition with potash. Yet it is necessary to perform the filtering and washing of the precipitate with the utmost diligence, for if left too long under the ammoniacal liquor, a portion of the oxyde would be redissolved, and the liquor would then assume a bluish tinge.

Carbonate of potash should not be employed to precipitate protoxyde of copper, for a small portion would then remain in solution, which could not be obtained except by evaporating the liquor to dryness, and slightly igniting the salt.

The method which consists in precipitating the copper in the metallic state, by plunging in its solution a bar of bright iron, does not yield an accurate result, because the copper, whilst drying, is converted into suboxyde of copper. It is also generally contaminated by some charcoal which the iron abandons whilst dissolving. This method is therefore resorted to only in certain cases.

\* If copper is contained in the metallic state in combinations, it must be dissolved in nitric acid or aqua regia. This solution always contains the copper in the state of protoxyde of copper, which may be precipitated as we have said, and from the weight of which that of the metallic copper can be determined.

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The French edition has the following remark by M. E. Peligot :—

“ Mr. Levol, by applying the method proposed by Fuchs for the quantitative determination of protoxyde and of peroxyde of iron by means of metallic copper, and also for that of that metal in the salts of copper, indicates the following process as yielding most accurately the quantity of copper contained in a protosalt of that metal. The solution of the salt is to be supersaturated by ammonia, and a blade of pure copper, most exactly weighed,

is plunged into the whole depth of the vessel which contains the blue liquor, and which has been filled up entirely with boiled water; this vessel, for which a glass-stoppered flask having a large mouth is preferable, is immediately closed up after the introduction of the blade of copper, and the experiment is left to itself until the liquor is completely decolorised in consequence of the reduction of the protosalt of copper into a subsalt of copper. The blade of copper is then weighed, previously washing and drying it, and from the loss of weight it has sustained, the quantity of the metal which existed in the solution may be estimated, since for the same quantity of oxygen suboxide of copper contains twice as much copper as protoxyde of copper.

“This method is simple and easy, but it has the drawback of being somewhat slow. About four days are required for the complete action of copper upon an ammoniacal protosalt of copper containing one gramme (about fifteen grains) of copper, and succeeds as well for the reduction of sulphate of copper as for those of nitrate or of chloride of copper; it is particularly applicable for the dosing of copper in the alloys which this metal forms with zinc, tin, and antimony.”<sup>1</sup>

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\* DETERMINATION OF SUBOXYDE OF COPPER.

If a substance contains suboxyde of copper, it must be dissolved in nitric acid, by which it is converted into protoxyde of copper, which is subsequently precipitated by solution of potash, and from the weight of which that of the suboxyde of copper contained in the substance is calculated.

When a solution contains subchloride of copper, it becomes converted, after some time in contact of the air and by the action of an excess of muriatic acid, also into protochloride of copper, from which solution it may be precipitated by solution of potash in the state of protoxyde of copper. It is more expeditious still

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<sup>1</sup> From the solution to be thus treated, all the metals capable of being precipitated by copper, and those which are not kept in solution by ammonia, must of course be first removed.—Ed.



to heat the subchloride of copper with dilute nitric acid, by which a solution of protochloride of copper and of nitrate of protoxyde of copper is obtained, from which the whole of the copper may be precipitated, by means of potash, in the state of protoxyde of copper.

SEPARATION OF PROTOXYDE OF COPPER FROM OXYDE OF  
BISMUTH.

The best reagent for separating protoxyde of copper from oxyde of bismuth, is carbonate of ammonia, an excess of which being added, dissolves the protoxyde of copper, and precipitates the oxyde of bismuth. The operator should not filter immediately after the addition of the carbonate of ammonia, but the whole must be left at rest, for some time, in a warm place, in order that the oxyde of bismuth may completely settle. It is advisable, whilst this oxyde is still moist on the filter, to pour a solution of carbonate of ammonia upon it, in order to remove the last traces of oxyde of copper, which is not easily attained. After which, it is dried and ignited; protoxyde of copper is precipitated from the filtered liquor by solution of potash, after having first volatilised the excess of carbonate of ammonia by a gentle evaporation, and added a small quantity of pure ammonia.

\* According to Sander, the separation of the oxydes of copper, and of bismuth, cannot be effected by carbonate of baryta.

\* When an alloy of copper and bismuth has to be analysed, the best is to heat and expose it to the action of a current of gaseous chlorine. Chloride of bismuth distils over, and there remains a mixture of subchloride, and of protochloride of copper. A pretty strong heat is required to volatilise completely the chloride of bismuth, which is received in water, to which a sufficient quantity of muriatic acid has been added, and into which it dissolves completely. A current of sulphuretted hydrogen is then passed through the liquor, by which means sulphuret of

bismuth is precipitated, and which is treated as we said (page 165). The protochloride of copper left behind is dissolved in water; nitric acid is added, to dissolve the subchloride of copper, and the protoxyde of copper is precipitated by solution of potash.

SEPARATION OF PROTOXYDE OF COPPER FROM PROTOXYDE  
OF LEAD.

\* The protoxyde of lead contained in a solution of protoxyde of copper is easily separated by boiling the solution with one of hydrate of potash. The protoxyde of copper which remains contains some protoxyde of lead, which no excess of potash can separate.

The method ordinarily adopted to separate protoxyde of copper from protoxyde of lead, is the following :—The two oxydes are dissolved in nitric acid, and sulphuric acid is added to the solution, evaporated to dryness, and towards the end the mass is heated, so as to volatilise the excess of sulphuric acid employed. Water is then poured upon the dry mass, which leaves insoluble sulphate of lead; this salt is collected on a filter, washed, dried, slightly ignited, and the quantity is then determined. Solution of potash is then poured in the liquor filtered therefrom, by which the protoxyde of copper is precipitated.

This filtered liquor contains still a very small quantity of sulphate of lead, which was first dissolved by the water, and then maintained in solution by the excess of potash. A sufficient quantity of acid is added to saturate the liquor, and then a small quantity of oxalate of ammonia, which precipitates this small portion of protoxyde of lead in the state of oxalate of lead.

\* Any liquid containing these two oxydes in solution may be treated in the same manner. Yet no ammoniacal salt should be present, because sulphate of ammonia is somewhat difficult to volatilise.

\* This method yields a more accurate result than when protoxyde of copper and of lead are separated from each other by carbonate of ammonia, for the carbonate of lead thus produced always contains a little protoxyde of copper, even though a

large excess of carbonate of ammonia has been employed, and owing to which, it has a greenish tinge. By pouring a solution of carbonate of ammonia upon the carbonate of lead, without removing the filter, a small portion of protoxyde of copper may be redissolved; but it is very difficult to eliminate it entirely.

\* Another method of separating protoxyde of copper from protoxyde of lead, consists in converting them both in the state of chlorides, by means of muriatic acid, and to separate the two ehlorides by means of strong alcohol, which leaves the chloride of lead undissolved, and which must be washed with alcohol. The protoxyde of lead cannot be precipitated from the alcoholic liquor by potash. The alcohol is first volatilised, the protochloride of copper is dissolved by a large quantity of water, and by means of a current of sulphuretted hydrogen passed through the liquor, sulphuret of copper is precipitated, which is converted into protoxyde of copper, by the process which will soon be described.<sup>1</sup>

#### SEPARATION OF PROTOXYDE OF COPPER FROM OXYDE OF CADMIUM.

According to Stromeyer protoxyde of copper may be separated from oxyde of cadmium by means of carbonate of ammonia, which must be in excess. Carbonate of cadmium is thereby precipitated, the protoxyde of copper remains dissolved with a little oxyde of cadmium. If this solution be exposed to the air, the oxyde of cadmium is gradually deposited in a complete

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<sup>1</sup> According to MM. Haidlen and Fresenius, protoxyde of copper and oxyde of lead may be separated from each other in the manner described before, when speaking of the separation of oxyde of cadmium from oxyde of bismuth. The double cyanide of copper and potassium must, in that case, be converted into protochloride of copper by boiling in muriatic acid with addition of nitric acid, after which the copper is precipitated, in the state of sulphuret of copper, by means of sulphuretted hydrogen.—The two metals may likewise be separated by cyanide of potassium when in the state of sulphurets, because sulphuret of copper is easily and completely soluble in cyanide of potassium, in which sulphuret of bismuth is insoluble.—Ed.

manner; the carbonate of ammonia volatilises, and the protoxyde of copper remains in solution.<sup>1</sup>

SEPARATION OF PROTOXYDE OF COPPER FROM THE OXYDES OF URANIUM, OF NICKEL, OF COBALT, OF ZINC, OF IRON, AND OF MANGANESE, FROM THE EARTHS AND FROM THE ALKALIES.

Protoxyde of copper may be very easily separated by sulphuretted hydrogen from all the oxydes, which this gas does not precipitate from an acid solution. The solution of the oxydes is first to be rendered acid, preferably by muriatic acid, after which a current of sulphuretted hydrogen is very slowly passed through it. The current must be continued until the liquor is perfectly saturated, and exhales a strong odour of the gas.

\* The sulphuret of copper which is precipitated by this treatment must be rapidly collected on a filter, and washed with water without interruption.' It is better, however, to wash it with water containing some sulphuretted hydrogen, for when sulphuret of copper is washed for too long a time with pure water, although the latter may pass clear through the filter, yet it very often turns brown when added to that which has been filtered from the precipitate. This phenomenon is owing to this, that recently precipitated sulphuret of copper absorbs a little oxygen when left in contact with the air, the oxydised portion dissolving in the water. When the solution is after-

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<sup>1</sup> According to MM. Haidlen and Fresenius (*Annal. der Chem. und Pharm.* Bd. lxxiii. heft. 2) copper may also be separated from cadmium by cyanide of potassium as follows: cyanide of potassium is added to the solution of the two metals, until the precipitate at first formed is redissolved. The solution contains then a double cyanide of copper and of potassium, and a double cyanide of cadmium and of potassium. A stream of sulphuretted hydrogen is then passed through it, by which the two metals are converted into sulphurets. The sulphuret of cadmium is completely precipitated, the excess of sulphuretted hydrogen is expelled by heat, and more cyanide of potassium is added, so that the whole of the sulphuret of copper remains in solution, which is then to be boiled with muriatic acid, nitric acid being added until all the hydrocyanic acid is expelled, and the copper is precipitated afterwards by potash.—En.

<sup>2</sup> Moist sulphuret of copper becomes gradually converted into sulphate of copper by exposure.—En.

wards mixed with the liquor which has been filtered from the sulphuret of copper precipitated, as this latter liquor contains still free sulphuretted hydrogen in solution, a small quantity of sulphuret of copper is again precipitated, which imparts a brown tinge to it. Nothing of the kind is apprehended when washing is performed with water which contains a little sulphuretted hydrogen, and is carried on without interruption.

\* Whenever the protoxyde of copper contained in an acid liquor has been precipitated therefrom by sulphuretted hydrogen in the state of sulphuret of copper, the precipitation is deemed complete, when, after having left off passing sulphuretted hydrogen through it, and removed the apparatus used for disengaging it, the sulphuret of copper produced exhales a strong odour of the gas.

As soon as the precipitation is complete, the operator must immediately proceed to filter it, because if the solution contains any nitric acid or aqua regia, and is not diluted too much, the acid, even in the cold, exercises an oxydising action upon the sulphuret of copper, a greater or less proportion of which dissolves after some time. Yet so long as the liquor exhales the odour of sulphuretted hydrogen, this does not take place, wherefore it is absolutely necessary that it should retain that odour during all the time that the filtering lasts.

The quantity of the protoxyde of copper contained in the solution cannot be calculated from that of the sulphuret of copper, because it becomes slightly oxydised whilst drying in the air. It is, therefore, necessary to convert it into protoxyde of copper, and the quantity of the latter is thus determined. The best way of effecting this, consists in drying the sulphuret of copper until it may be easily detached from the filter, and it is put in a glass. The filter, which still contains a small quantity of it, is carefully burnt upon the cover of a platinum crucible, and the ashes are added to the sulphuret. Nitric acid, or better still, aqua regia, is poured upon the whole, and left to digest until all the sulphur liberated has a pure yellow

colour, which takes place in a short time. The solution is filtered, to separate the sulphur which is to be washed, and the protoxyde of copper is precipitated by means of solution of potash.

The sulphuret of copper may also be converted into protoxyde of copper, by drying it to a certain extent upon the filter, roasting it with the contact of the air in a platinum crucible until the flame of burning sulphur has ceased; the residuum is dissolved in an acid, and the oxyde is precipitated from the liquor by means of a solution of pure potash. The filter upon which the sulphuret of copper has been collected, must in this case be burnt in the usual way in the platinum crucible. As a certain portion, more or less, of suboxyde of copper is always formed during the roasting of the sulphuret, it is advisable to add some hot nitric acid to the solution of the roasted residuum. A further quantity of unoxysed sulphur is thus often separated again, which must be collected on a filter. Yet this method does not answer the purpose so well as the one which has just been described.

When, even immediately after the washing, the still moist sulphuret of copper, together with the filter, is digested in nitric acid or aqua regia, and especially if the digesting lasts long, and under the influence of a somewhat strong heat, the action of the acid upon the paper produces an organic substance which prevents the subsequent precipitation of the protoxyde of copper by potash from being complete. Yet if the digestion of the sulphuret of copper is effected at a gentle heat only, and does not last longer than is necessary to allow of the sulphur acquiring a yellow colour, the oxyde of copper may be completely precipitated by potash.

\* But if the filter and sulphuret of copper have been inadvertently left too long in digestion with the acid, and there be reason to fear that the solution of potash will not be able to precipitate the whole of the protoxyde of copper from the solution, the latter should be precipitated anew by means of sulphuretted hydrogen, or, which is better, sulphuric acid should

be added to the liquor, and the whole exposed to a gentle heat and evaporated to dryness, or, at any rate, until it has ceased to disengage nitric acid fumes. The sulphuric acid chars the organic matter in solution, and as the liquor is gradually concentrated by evaporation, it gradually oxydises the greatest portion of the charcoal at first liberated. The operation being at an end, the sulphate of copper produced is dissolved in water, and the protoxyde of copper is precipitated from the liquor by means of solution of potash.

Protoxyde of copper may also be completely precipitated from neutral or ammoniacal solutions by means of *hydrosulphuret of ammonia*. The sulphuret of copper which is thus precipitated, is completely insoluble in any excess whatever of ammonia and of hydrosulphuret of ammonia; <sup>1</sup> but it oxydises in the air more rapidly still than that which has been precipitated from an acid solution by sulphuretted hydrogen, wherefore it must be washed with water containing some hydrosulphuret of ammonia. After washing, it is treated like that which has been precipitated by sulphuretted hydrogen.

Protoxyde of copper being very soluble in *ammonia*, this reagent is generally resorted to, to separate it from substances which are completely precipitated by ammonia. This method is often employed to separate peroxyde of iron from protoxyde of copper; but the peroxyde of iron thus precipitated, retains still a pretty considerable quantity of protoxyde of copper, which cannot be eliminated by any excess whatever of ammonia, at least completely. Sulphuretted hydrogen is, therefore, to be preferred.

Oxydes which are soluble in a solution of *potash*, often cannot be separated from protoxyde of copper by this reagent. Thus, for example, oxyde of zinc cannot be separated from protoxyde

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<sup>1</sup> This is an error. Sulphuret of copper is perceptibly soluble in hydrosulphuret of ammonia; but it is completely insoluble in sulphuret of potassium.—ED.

of copper by means of solution of potash, whatever be the excess employed. The protoxyde of copper is precipitated, it is true, in a complete manner, but it contains oxyde of zinc, which falls down with it. It would, therefore, be quite wrong, in the quantitative analysis of brass, to treat the solution by potash. The separation of the two oxydes is easily and completely effected, by passing a current of sulphuretted hydrogen through their somewhat strongly acidified solution.<sup>1</sup>

*Sulphuretted hydrogen* is the reagent employed to separate protoxyde of copper from the oxyde of uranium, of nickel, of cobalt, of iron, and of manganese, in acid solutions. The same reagent is likewise employed to separate it from oxyde of zinc, yet the solution, in that case, must be rendered a little more acid, in order to prevent some sulphuret of zinc from being precipitated along with the sulphuret of copper. Lastly, sulphuretted hydrogen is employed also to separate protoxyde of copper from the earths and from the alkalies.

SEPARATION OF PROTOXYDE OF COPPER FROM THE OXYDES  
HITHERTO TREATED OF, AND FROM PROTOXYDE OF LEAD.

If protoxyde of lead and of copper have to be separated from the oxydes which have been enumerated, the two metals are precipitated together in the state of sulphurets, by passing a current of sulphuretted hydrogen through the acid solution, for

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<sup>1</sup> The following process may serve for analysing brass in the dry way : Prepare a small hessian crucible about two inches high by one inch and a half wide, and put at the bottom a layer of lamp-black well pressed, and into this put about 20 gr. of the brass to be analysed, and fill the crucible over it with lamp-black or charcoal powder, put the cover on and lute it well with clay. The crucible is then exposed to a red heat, and kept at that temperature for several hours, after which it is withdrawn and allowed to cool. It is then opened and its contents are poured in a glass ; the charcoal is removed by blowing with a pair of bellows, the alloy is weighed, and submitted to the same operation again, until two consecutive weighings agree. The weight of the last operation is that of the pure copper, and the loss indicates that of the zinc. The copper thus obtained, however, is contaminated by a small portion of carburet of copper.—Ed.



which purpose, in the present case, nitric acid deserves the preference. After having dried the two oxydes, they are treated by concentrated and fuming nitric acid, as has been said (page 162), when speaking of sulphuret of lead alone. The whole is evaporated to dryness, and the sulphate of copper is separated from the sulphate of lead, by treating the slightly ignited residuum with water (page 183).

## CHAPTER XXIV.

## SILVER.

## DETERMINATION OF SILVER AND OF OXYDE OF SILVER.

OXYDE of silver is more easily separated from other substances, and is quantitatively determined in a more rigorous manner than many other oxydes. When it is contained in a solution, it is precipitated therefrom by muriatic acid, in the state of chloride of silver, which is insoluble. The only precaution to be taken during this operation, consists in rendering the solution acid before precipitating it, which may be done by means of nitric acid. The chloride of silver produced by the reaction is not so easily deposited when the liquor is neutral, and it must not be ammoniacal, for, in presence of an excess of ammonia, not a single particle of chloride of silver would be precipitated. If the solution of oxyde of silver is very concentrated, it should not be treated by very strong muriatic acid, because an excess of this acid might dissolve a little of the chloride of silver, which, however, would be immediately reprecipitated by dilution with water.

Muriatic acid is a more accurate reagent for precipitating oxyde of silver, than chloride of potassium, of sodium, or muriate of ammonia; the latter especially, when added in large quantities, may dissolve the last traces of chloride of silver. If, by precipitating chloride of silver, it is impossible to prevent the formation of a large quantity of muriate of ammonia, or of chloride of potassium, or of sodium, which may very easily take

place, it is advisable, according to Gay Lussac and Liebig, to begin by evaporating the liquor filtered from the chloride of silver, almost to dryness, and to pour nitric acid on the residuum; by heating the whole, the chlorides of the alkalisable metals are converted into nitrates, whilst the small quantity of chloride of silver remains unaltered, and does not dissolve by diluting the liquor with water.

Before filtering the liquor from the chloride of silver, it is advisable to heat the whole moderately, because the chloride of silver deposits better then. Yet, even without heating, the chloride of silver is completely precipitated after some time; in all cases, however, the whole should be left at rest about twelve hours before filtering. The filtering being finished, the precipitate must first be washed with water to which a small quantity of nitric or of muriatic acid has been added; for if pure water was employed, it would often happen, that at first a little chloride of silver would pass through the filter, and form a white cloud in the filtrate, which, however, passes clear afterwards. Yet the water employed for washing does not always turn milky. This does not take place when the liquor has been strongly heated before filtering, but it may always be avoided by rendering the first water used for washing slightly acidulous, or, better still, by filtering the liquor from the chloride of silver, pouring hot water on the latter in the glass in which it has been precipitated, stirring the whole well, allowing it to subside, pouring the water on a filter, and again pouring hot water upon the chloride of silver until it is completely washed in the glass itself; when it is then thrown upon the filter, the liquor ordinarily passes clear.

Chloride of silver must be washed on as small a filter as possible. After washing, it must be dried with great care, and introduced into a counterpoised porcelain crucible, and the filter is scraped as clean as possible, and burnt upon the cover of the platinum crucible, which is used afterwards to close the porcelain crucible into which the chloride of silver is to be fused, and, after cooling, it is weighed. When the chloride of silver

has not been thoroughly dried, a projection often takes place during the ignition, which may prove a source of loss. From the weight of the chloride of silver obtained, the quantity of the oxyde of silver, or of the silver, is calculated.<sup>1</sup>

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\* The following note is by M. E. Peligot:—

“ The chloride of silver may also be collected and dried upon a counterpoised filter, and weighed upon that filter; but as the filtering paper often loses some of its weight by washing it with acid liquids, by reason of the carbonate of lime contained therein, and which is then dissolved, the operator must take care to employ a filter previously washed with very dilute nitric acid; and in order to diminish as much as possible the error which may result from the hygrometric property of paper, it is advisable to employ, as a counterpoise of the paper, another filter of the same paper washed with the same acidulated water, and dried in the same manner. The chloride being collected, the filter containing it is dried at the same time, and along with the filter used as a counterpoise. This method is not very exact, but I think that the one which consists in burning the filter, as has been just developed, may be a source of greater error, by reason of the reduction and volatilisation of a portion of the chloride of silver; and, moreover, it is of a more easy execution. The best process is that proposed by M. Marignac, and which is as follows:—The chloride of silver is collected in a counterpoised tube two centimetres in diameter [see at the end of this volume], and drawn to a point at one extremity. The curdy precipitate is soon arrested by the point of the tube, yet without impeding the filtering; the liquor passes perfectly clear if the operator takes care to add a little nitric acid to the

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<sup>1</sup> According to M. Mohr the chloride of silver may be reduced into metallic silver by ignition with rosin. Chloride of silver is mixed with half its weight of rosin, and moderately heated in a crucible until the flame ceases to have a greenish blue colour; the fire is increased towards the end, in order to fuse the reduced silver into a metallic button.—ED.

liquor used for washing. The tube is wrapped in black paper, and the chloride remains white during all the time employed in washing; when the washing is finished, the chloride is dried by introducing the tube which contains it into a larger tube of metal, which is heated in an oil bath, and when dry it is weighed. By closing with the spirit-lamp the drawn out point of the tube, and fusing the chloride dried as just said, it does not undergo any change, provided it was thoroughly dry.”—

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SEPARATION OF OXYDE OF SILVER FROM THE OXYDES OF THE  
OTHER METALS.

By *muriatic acid* not only can oxyde of silver be completely precipitated from a solution, but it may thus be separated from all the oxydes hitherto treated of, for all the metals of these oxydes form with chlorine, compounds which are soluble in water. Even protoxyde of lead may very well be separated from oxyde of silver by means of muriatic acid, but the solution must, in that case, be diluted with a very large quantity of water before adding the muriatic acid, because chloride of lead is very sparingly soluble in water, and, moreover, a large excess of muriatic acid should be avoided, because chloride of lead is much less soluble in that acid than in pure water alone.

\* According to Döbereiner, chloride of silver, may also be separated from protoxyde of copper by means of a *formiate of alkali*, when these two oxydes exist in the state of nitrates in a suitably diluted solution. The whole is heated until carbonic acid is no longer disengaged, the oxyde of silver is reduced into metallic silver, which is put aside, and the protoxyde of copper remains in solution.<sup>1</sup>

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<sup>1</sup> MM. Haidlen and Fresenius recommend also the use of cyanide of potassium for separating silver from copper, as follows : Cyanide of potassium is added to the solution of the two metals until the precipitate redissolves. A current of sulphuretted

Oxyde of silver may be completely separated from an acid solution by means of *sulphuretted hydrogen*, and from an ammoniacal solution by means of *hydrosulphuret of ammonia*. Yet this method of precipitating oxyde of silver is ordinarily resorted to only when the object is to separate it from substances which will be subsequently treated of, though it may very well be separated from the oxydes of uranium, of nickel, of cobalt, of zinc, of iron, and of manganese, also from the earths and from the alkalies by means of sulphuretted hydrogen, when the solution which contains it is acid.

The sulphuret of silver produced by sulphuretted hydrogen, is collected on a filter, dried, weighed, and from its weight the quantity of the silver is calculated. If, however, the operator has reason to think that sulphur has precipitated with the chloride of silver, which takes place, for example, if the solution contained peroxyde of iron at the same time, the chloride and the filter should be dissolved in pure nitric acid until all the liberated sulphur has acquired a yellow colour; the solution is then filtered, and the silver is precipitated therefrom by means of muriatic acid in the state of chloride of silver. As to the sulphuret of silver, precipitated by hydrosulphuret of ammonia, it should always be treated as just described.

When the alloys of silver with other metals have to be analysed in the humid way, they may be completely dissolved in nitric acid and the oxyde of silver may be precipitated from the solution by means of muriatic acid, or else aqua regia may at once be employed; the chloride of silver remains then insoluble, after diluting the liquor with water.

\* The first of these methods, however, is preferable,—that is

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hydrogen is now passed through the solution, and the excess of the gas is expelled by heat, and a little more cyanide of potassium is then added, by which means the whole of the silver is precipitated whilst the copper remains in solution. Or else an excess of nitric acid is added to the solution of the two cyanides in cyanide of potassium, by which means the cyanide of silver is precipitated, whilst the cyanide of copper is thereby decomposed, the copper thereof being at the same time dissolved; the liquor is boiled until all the hydrocyanic acid is expelled, and the copper is then precipitated by potash.—Ed.

to say, dissolving first the metals in nitric acid, and then precipitating the solution by muriatic acid; for when an alloy containing a pretty large quantity of silver is treated by aqua regia, it becomes immediately covered by a crust of chloride of silver, which altogether prevents the aqua regia from acting on the as yet unattacked portions of the alloy. It is true that the liquor might be decanted, the crust of chloride of silver dissolved by ammonia, and after decanting the solution, the remainder of the alloy might be treated by a fresh portion of aqua regia, but as the operation would have to be repeated a great number of times, which would make the operation a long and tedious one, it is better to limit this method to such alloys only which contain little silver.

When, however, the operator has to determine the quantity of silver contained in certain alloys, especially in those which this metal forms with copper, lead, and other comparatively valueless metals, the method called *cupellation* is ordinarily resorted to. The essential object of cupelling is the oxydisation of the baser metals alloyed with the silver, by heating the alloy in contact with the air. Pure lead is added, which becomes likewise oxydised, and which, when oxydised, combines with the oxydes of the other metals, so as to form a fusible mass, which then sinks into the pores of the cupel, whilst the silver remains in the reguline state, and may be quantitatively determined after cooling. This method often yields a result which is sufficient for technical purposes, although a small quantity of silver generally penetrates into the pores of the cupel with the oxydes of the baser metals. The quantity of the other metals contained in the alloy cannot be thus appreciated. As this method is very complicated, and the precautions to be observed, when put in practice, are indicated in a great many chemical and technological works, I may suppress here the details of this operation, the more especially as for rigorously accurate determinations this method cannot be adopted, because, in point of exactness, it is much inferior to that in the humid

way. When, however, a very complex substance contains an extremely feeble quantity of silver, the most exact manner of determining it is by cupellation, especially when the silver in the combination is only in an exceedingly minute proportion.<sup>1</sup>

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<sup>1</sup> According to MM. Haidlen and Fresenius, silver may be separated from lead by cyanide of potassium, as follows :—Solution of cyanide of potassium is added to that of the two metals, and heat is applied. The lead remains as residuum, and the silver is reduced in the state of double cyanide of silver and of potassium, which is to be decomposed by nitric acid ; nitrate of potash is formed, and cyanide of silver is precipitated, from the weight of which that of the silver is estimated.—Ed.



## CHAPTER XXV.

## MERCURY.

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THE ordinary way of determining mercury in quantitative analysis consists in reducing it from its solutions, and *protochloride of tin* is the reagent ordinarily employed to effect this reduction. A solution of *phosphorous acid* is however a more advantageous reagent, or else the acid which results from the deliquescence of phosphorus in moist air. But as protochloride of tin is more easily procurable in large quantities than phosphorous acid, the former is more frequently employed.

Whether the mercury exists in the solution in the state of protoxyde or of suboxyde, of chloride or bromide of mercury, is a matter of indifference. The liquor might also contain free muriatic acid, dilute sulphuric acid, or other acids, without inconvenience, but it must not contain any nitric acid, or if this latter exists in it, peculiar precautions must be observed. It is not even necessary that the substance which contains mercury should be soluble in water or in muriatic acid, in all cases protochloride of tin reduces the mercury in the metallic state from the insoluble salts of mercury, but not from the sulphurets, as may be easily conceived.

The methods employed to perform these operations are the following:—If the substance which contains the mercury is insoluble, it must be put in a matras, and concentrated muriatic acid is poured upon it, and a concentrated solution of protochloride of tin, previously mixed with enough muriatic acid to render it

perfectly clear, is added. Instead of adding muriatic acid, the solution may be filtered. The whole is then boiled, but the boiling must not last more than a few minutes, because, if continued for a longer time, mercurial fumes might be disengaged with the aqueous vapour. The flask or matrass is then closed up, and the whole is suffered to cool. The mercury is then completely reduced at first under the form of a black precipitate, consisting of extremely divided globules, but which, by a prolonged ebullition, coalesce into larger ones.

After cooling, the clear supernatant liquor is decanted from the globules of mercury, which are then to be washed, without filtering, with water slightly acidulated with muriatic acid, and the washing is continued until the metallic mercury is freed from all foreign substances. The moist mercury is then shaken into a small counterpoised platinum crucible, and the greatest part of the moisture at the surface is absorbed with blotting paper, after which it is completely dried and then weighed. The drying must be performed by exposure to the air only, and not in a warm place, even if the temperature were moderate.

If the black precipitate will not unite into larger globules, the supernatant liquor is decanted and boiled for some time with muriatic acid, which will immediately determine the formation of larger globules. It very frequently occurs, that layers of mercurial globules swim at the surface of the liquid; in which case the operator must endeavour to wet them by agitation, by which means they are made to sink to the bottom. The liquors separated by decantation from the reduced mercury are put aside in a glass, with the water used for washing, from which it often happens that traces of reduced mercury, which were held in suspension separate; these traces are carefully collected and added to the principal mass of the metal.

\* When the vessels in which the reduction of the mercury is effected by means of protochloride of mercury are not scrupulously clean, and if their inner sides are covered with an extremely thin and imperceptible film of grease, the mercurial globules obtained have not a metallic appearance. As this circumstance

may frequently take place in laboratories, it is advisable to rinse these vessels with a few drops of solution of potash, in order to remove all the grease.

If mercury is contained in a dilute solution, the liquid must first be acidified by adding muriatic acid to it, after which a solution of protochloride of tin, rendered clear by means of muriatic acid, is poured in, and the whole is boiled for a few minutes. In such cases the mercury seldom unites in large globules, and ordinarily it only forms a black precipitate. The clear liquor is separated from the mercury, concentrated muriatic acid is poured upon the latter, and heat is applied; large globules of mercury are ordinarily formed immediately by this treatment.

The black precipitate must not be left at rest for more than twenty-four hours, because otherwise large globules could not be obtained by treatment with muriatic acid. The obstacle to the immediate formation of large globules in a dilute liquor, is owing principally to a small quantity of peroxyde of tin produced during the operation, and which is precipitated at the same time with the mercury; concentrated muriatic acid dissolves this oxyde, it is true, but it is difficult to effect this solution when the whole has been left at rest for too long a time.

The determination of mercury by this method becomes uncertain when the liquor contains nitric acid. It is then necessary gradually to add muriatic acid to the solution, and to concentrate it by heat. The nitric acid is destroyed thereby, chlorine and muriatic acid being at the same time set at liberty and volatilised. The addition of the muriatic acid in the hot solution, must, therefore, be continued so long as an odour of chlorine is evolved. A solution of protochloride of tin is then poured in the liquor, and the operation proceeds as we have just said.

\* When the solid compound to be analysed contains mercury and likewise nitric acid, it is easy to destroy it (the nitric acid) by means of concentrated muriatic acid; but if the solution from which the mercury is to be quantitatively determined, contains

a considerable proportion of mercury, it is difficult, in spite of all possible precaution, to obtain the quantity of the metal in an exact manner. In such a case it is better to employ sulphuretted hydrogen for the purpose of precipitating the mercury in the state of sulphuret, from which the quantity of the metal is to be determined, as will be shown subsequently.

If phosphorous acid, or the acid which results from the deliquescent of phosphorus, is employed to effect the reduction of mercury, the process is about the same as when protochloride of tin is used, but the large globules of mercury are much more easily obtained than with the salt of tin. Phosphorous acid may also be used when the liquor operated upon contains nitric acid, provided a sufficient excess of it be employed; for nitric acid is more readily destroyed in the hot way by phosphorous acid, than by muriatic acid. On this account phosphorous acid should always be preferred to protochloride of tin, but it cannot be procured so easily in great quantity as the latter reagent.

\* In the determination of mercury as metal, an unavoidable loss always takes place, and which, when operating upon large quantities, may often amount to nearly one per cent. A better method of determining mercury in compounds, consists in converting it into subchloride of mercury, which may be dried upon a weighed filter, after which its weight may be very accurately determined.

\* The best method of precipitating mercury in the state of subchloride of mercury, is formiate of potash or of soda, this reagent having the further advantage, that the presence of nitric acid does not prevent the precipitation from taking place. If the mercury is combined with a metallic compound, it should be dissolved in aqua regia. If it exists in the state of oxyde in a nitric acid solution, muriatic acid should be added thereto. In either case the liquor should be saturated with a solution of hydrate of potash, but in such a way that it still remains slightly

acid. A solution of formiate of potash or of soda is then added, and the whole is left exposed for several days, at a temperature of about  $60^{\circ}$  or  $80^{\circ}$  centig., under the influence of which, according to Bonsdorff, the mercury separates completely in the state of subchloride of mercury. The operator should, however, be very careful not to elevate the temperature beyond  $80^{\circ}$  centig., because at the boiling point of water the protoxyde of mercury would be reduced into metallic mercury. But it is safer to employ a lower temperature, for example, from  $50^{\circ}$  to  $60^{\circ}$  centigrade, only the separation of the subchloride of mercury requires a longer time.

The subchloride of mercury obtained is collected upon a weighed filter; some formiate of alkali is added to the filtered liquor, which is still left for twenty-four hours at the temperature at which the precipitate has been produced; by which means a small quantity of subchloride of mercury is often separated again, which is added to the other. The salt should not be dried before the operator has well ascertained that the liquor deposits no more of it. In order to be sure that the whole of the mercury has been precipitated, the liquor may be tested with a little sulphuretted hydrogen. The chloride is then dried by a very gentle heat until its weight remains constant.

The reduction by the humid way is the best and most exact method of determining the quantity of mercury in a substance under examination; the other methods are not quite accurate. Thus, for example, peroxyde of mercury cannot be completely precipitated from its solutions by alkalies.

The quantity of mercury contained in a substance may often be determined by separating it from the other constituents by distillation. This method, however, requires many precautions; and even then, however careful the operator may be, it does not yield results so accurate as by the humid way. The operation should be conducted as follows:—The substance which contains the mercury is put in a small retort, and if the mercury exists in the state of oxyde, of oxysalt, or of sulphuret, it is mixed

with carbonate of alkali or with pure lime ; but as glass is much attacked by alkalies, lime is preferable ; it is best, however, to employ both lime and potash conjointly, bearing in mind the other substances which may be required to be quantitatively determined in the residuum. This being done, the neck of the retort is to be drawn out into a long tube, which, however, must not be too thin ; and it is then introduced into a small receiver containing a sufficient quantity of water, so that the neck of the retort reaches immediately the surface of the liquid. If the neck of the retort were to plunge into the water, there would be danger of absorption, and the water would ascend into the retort if, during the distilling process, the heat should come to decrease. If the retort is very small, the distillation may be carried on with an argand spirit-lamp ; yet it is better to employ a small furnace, but then it is necessary to moderate the heat so as not to soften or fuse the glass.

The distilled mercury condenses at the bottom of the receiver under the water contained therein. When the operator has taken care to cool the exterior of the receiver during the operation, there is no fear of losing a portion of the metal in the state of fumes. After cooling, the neck of the retort is cut near the body of the retort, and the globules of mercury, which adhere to the neck, are washed down by a stream of water. The mercury is then dried in the air and weighed. If the combination containing mercury is very volatile,—for example, if it consists of protochloride of mercury [corrosive sublimate] or subchloride of mercury [calomel] it almost always happens that the heat volatilises a portion of the substance before the alkali has had time to effect the decomposition, especially if the mixture has not been carefully and intimately made. In such a case, it is advisable after having mixed the mercurial compound with the alkali to moisten the whole thoroughly with water, and to leave it at rest for some time. The result is a decomposition, owing to which protoxyde of mercury is separated, which the action of heat alone decomposes into mercury and oxygen.

Nothing of the kind need be apprehended when the mercury exists in the substance in the state of oxyde or of sulphuret. It is worthy of remark, that by operating in this manner a little more mercury, in weight, is obtained than should be.

If the mercury is combined in a metallic compound with metals which are not volatile, the quantity can very often be determined in an accurate manner by exposing the amalgam to a red heat, which volatilises the mercury, whilst the fixed metals remain behind, and their weight being ascertained, the loss indicates that of the mercury. If the metals left behind are not oxydised by exposure to the air, the experiment may be performed in a small porcelain crucible by means of an argand spirit-lamp; if they are oxydisable by exposure to the air, under the influence of a high temperature, the ignition should be effected in a small retort, the neck of which, after the volatilisation of the mercury, is closed by fusing it whilst the body of the retort is still red hot.

**\* DETERMINATION OF SUBOXYDE OF MERCURY.**

If this oxyde is contained in a solution it may be precipitated by dilute muriatic acid, and determined in the state of subchloride of mercury. A necessary condition here is that the liquor be very dilute and contain as little free nitric acid as possible, because this acid might convert a small quantity of subchloride into perchloride of mercury, which would remain in solution.

**SEPARATION OF THE OXYDES OF MERCURY FROM OXYDE OF SILVER.**

Peroxyde of mercury may be completely separated from oxyde of silver by means of muriatic acid, which precipitates only the latter of these two oxydes. After having filtered the liquor, to separate the chloride of silver, the mercury may then be precipitated by one of the methods which have been just described.

When a combination of oxyde of silver and of suboxyde of mercury has to be analysed, the latter should be converted into

peroxyde of mercury, which in most cases may be done by digesting the dry substance, or its solution, in nitric acid, with the help of heat.

\* In metallic compounds, and even in certain combinations of oxydes, the mercury may be volatilised by heat, the silver being thus left behind in a pure state.<sup>1</sup>

#### SEPARATION OF THE OXYDES OF MERCURY FROM PROTOXYDE OF COPPER.

According to Bonsdorff, the best method of separating protoxyde of copper from the oxydes of mercury is the following : To the solution of the oxydes (if the mercury exists in the state of suboxyde of mercury, it should be first converted into peroxyde by means of nitric acid) add muriatic acid, and saturate the solution by potash, after which the mercury is precipitated as subchloride of mercury, as we have said (page 203). A solution of potash is then employed to precipitate the protoxyde of copper from the filtered liquor.

If the oxydes are in the dry state, and accompanied by other substances, it is very easy to find the quantity of protoxyde of copper in the mixture, by igniting a given weight of it in a platinum crucible ; the protoxyde of copper remains behind and the peroxyde of mercury volatilises, partly as metallic mercury, and partly as oxygen ; from the loss sustained, the quantity of the mercury may be known.

#### SEPARATION OF PEROXYDE OF MERCURY FROM PROTOXYDE OF LEAD.

If the operator has to analyse a dry compound of peroxyde of mercury (*oxyde mercurique*) and of one of the oxydes of lead,

<sup>1</sup> Cyanide of potassium may also be used, according to MM. Haidlen and Fresenius, for separating mercury from silver, and the process is the same as has been already several times alluded to, namely : The mercury, if not already in that state, must be converted into peroxyde of mercury, and to its solution cyanide of potassium is added, until all the precipitate is redissolved ; the liquor contains then a mixture of a double cyanide of silver and of potassium, and of cyanide of mercury and of potassium. An excess of nitric acid is added thereto, which decomposes the two



the following process may be resorted to : Muriatic acid is to be poured on the compound, and the whole is heated, which produces chloride of lead and perchloride of mercury. If the compound contains any peroxyde of lead instead of protoxyde of lead, chlorine is disengaged. Strong alcohol is now added, which dissolves the perchloride of mercury, and leaves the chloride of lead, which is then collected on a counterpoised filter, washed with alcohol, dried and weighed. The alcoholic solution of perchloride of mercury is then diluted with water, the alcohol volatilised by applying a very gentle heat, and the mercury is then precipitated by one of the methods which have been indicated above.

When the oxydes of lead and of mercury are combined in a solution with an acid capable of being expelled by muriatic acid, this method may also be employed. The muriatic acid is then poured in the solution, evaporated to dryness, and the residuum treated by alcohol.

*Another method* of separating oxyde of lead from peroxyde of mercury consists in adding sulphuric acid to the solution of the two oxydes, which forms a precipitate of sulphate of lead. The quantity of sulphuric acid should not be too small, for in such a case the addition of water would produce a yellow basic sulphate of peroxyde of mercury which is not dissolved by very dilute sulphuric acid. When this basic salt has formed, the supernatant liquor should be decanted, and the residuum is heated with a little sulphuric acid diluted with only from three to five parts of water, and water may then be added. The sulphate of lead produced is to be washed with water mixed with a little dilute sulphuric acid.

Peroxyde of mercury may also be separated from oxyde of lead by *another method*, which will be spoken of farther on.

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cyanides, and converts all the cyanide of potassium into nitrate of potash. The cyanide of silver is precipitated, and the cyanide of mercury remains in solution; the former is separated by filtering, and the mercury is precipitated from the filtrate by sulphuretted hydrogen.—Ed.

SEPARATION OF THE OXYDES OF MERCURY FROM OXYDES OF  
BISMUTH AND OF CADMIUM.

No accurate method is as yet known of separating oxide of bismuth and oxide of cadmium from the oxides of mercury, or metallic bismuth and cadmium, from metallic mercury. These two oxides not being reducible by protochloride of tin, nor by phosphorous acid, the peroxide of mercury might thus be determined in the substance under examination. In such a case, phosphorous acid is preferable to protochloride of tin, because sulphuretted hydrogen may then be resorted to for precipitating the oxides of bismuth and of cadmium from the liquor filtered from the reduced mercury, and they may then be subsequently determined by one of the methods described before.

\* Oxide of cadmium may be accurately separated from peroxide of mercury by means of formiate of alkali in the same manner as for separating it from protoxide of copper.

SEPARATION OF THE OXYDES OF MERCURY FROM THE OXYDES  
OF URANIUM, OF NICKEL, OF COBALT, OF ZINC, OF IRON,  
AND OF MANGANESE, FROM THE EARTHS AND FROM THE  
ALKALIES.

Whether mercury exists in a solution in the state of suboxide, of peroxide, or of chloride, it may be completely precipitated therefrom by *sulphuretted hydrogen* even when the liquor is acid. This method may therefore be resorted to for the purpose of separating the oxides of mercury from those of uranium, of nickel, of cobalt, of zinc, of iron, and of manganese, also from the earths and from the alkalies, these latter substances not

<sup>1</sup> MM. Haidlen and Fresenius separate mercury from cadmium and bismuth by cyanide of potassium, which is to be added to the solution of these salts until the precipitate is redissolved; dilute nitric acid is then added, and the whole is boiled. The cyanide of mercury is not thereby decomposed, whilst the cyanide of cadmium and the cyanide of potassium are converted into nitrates. After having eliminated the hydrocyanic acid the cadmium is precipitated by carbonate of potash, and the mercury is separated from the solution by sulphuretted hydrogen.—Ed.

being susceptible of precipitation from an acid solution by sulphuretted hydrogen.

If the solution be one containing suboxyde of mercury, a black precipitate of sulphuret of mercury is immediately produced, but those which contain peroxyde or perchloride of mercury yield the pure and black sulphuret of mercury only when the current of sulphuretted hydrogen has been passed through it for a considerable time; at the beginning, combinations of the persalts of mercury with sulphuret of mercury, of a white colour, are produced, but which are completely converted into sulphuret of mercury by a larger quantity of sulphuretted hydrogen.

If the operator is sure that the solution contains only peroxyde or perchloride of mercury, and no suboxyde of mercury, the quantity of the mercury may very well be calculated from that of the sulphuret obtained; but to do this, it is absolutely necessary that the solution should contain no peroxyde of iron, for the sulphuret of mercury would then be mixed with free sulphur. The sulphuret of mercury obtained is then dried at a very gentle heat, until, after successive weighings, the weight remains constant.

The sulphuret of mercury in the minimum of sulphur which sulphuretted hydrogen precipitates from the solutions of subsalts of mercury cannot be determined with the same accuracy, because a very gentle heat is already sufficient partly to decompose it, and to convert it into sulphuret of mercury in maximum of sulphur and metallic mercury. Now, as metallic mercury is perceptibly volatilisable at a very moderate heat, the precipitated sulphuret of mercury in minimum of sulphur always loses a little of its weight by drying, however low may have been the heat employed to effect this.

If the operator is not quite certain that the precipitate produced by sulphuretted hydrogen is pure sulphuret of mercury in maximum of sulphur, or if he be unwilling to determine the quantity of the mercury from the weight of this sulphuret, the sulphuret itself must be submitted to analysis.

The best method to effect this is the following :—The sulphuret of mercury is collected on a small filter, the paper of which must not be too thick, and it is washed thereon ; it is then to be introduced, whilst moist, along with the filter in a pretty large flask with a wide mouth and capable of being closed with a glass stopper ; muriatic acid, slightly diluted, is poured upon it, and in sufficient quantity to fill about one-twelfth part of the flask ; a slow current of chlorine gas is then passed through it, which gradually decomposes the sulphuret of mercury completely. The mercury combines with the chlorine, and forms perchloride of mercury, which remains in solution in the liquor, whilst a portion of the sulphur is converted into sulphuric acid ; another portion of this sulphur remains undissolved, and would be taken up only by continuing the action of the current of chlorine gas for a long time ; but the disengagement of the chlorine is stopped as soon as the undissolved sulphur has assumed a yellow colour. The disengagement-tube is then withdrawn from the liquor, washed carefully with water, and the flask is exposed to a very gentle heat, which dissipates the free chlorine. After cooling, the liquor is separated from the sulphur by filtering and the latter is washed ; as to the filtered solution, the mercury which it contains may be determined either by reduction with phosphorous acid or protochloride of tin, or, better still, by means of a formiate of alkali.

This method may likewise be employed when the liquor which contains mercury contains also a great quantity of nitric acid, which, as we have already said before, interferes with the accuracy of the immediate determination by means of protochloride of tin.

When the liquors operated upon are neutral or alkaline, the mercury may be completely precipitated, but only in the cold, by hydrosulphuret of ammonia, an excess of which, at a low temperature, does not dissolve the sulphuret of mercury. Yet it is advisable to treat the mercury thus obtained by chlorine, in order to convert it into perchloride of mercury, which may be next reduced into subchloride of mercury by means of a formiate

of alkali; from the quantity of the subchloride that of the mercury is calculated. In such a case the calculation of this quantity from the weight of the sulphuret of mercury would yield a less accurate result.

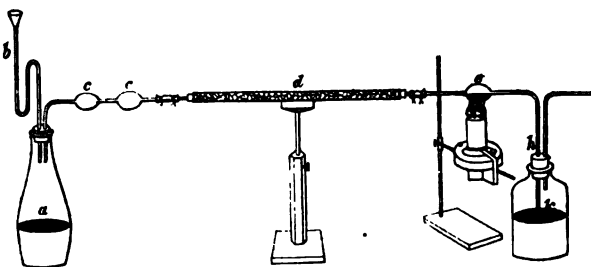
\* Mercury may be easily separated from all the non-volatile oxydes, by heating the mixture as we have said above, by which means the peroxyde of mercury becomes converted into metallic mercury and oxygen, both of which are volatilised by heat. If the oxydes are contained in the liquor in the state of dissolved salts, they might be precipitated by hydrosulphuret of ammonia in the state of sulphurets, which might be heated, after drying, in a small porcelain crucible, in order to volatilise the mercury, the others remaining behind. In such a case, the operator cannot obtain immediately the mercury from the oxyde or the sulphuret of mercury. In order to obtain this result, they must be heated in a small retort, and even then the exact determination of the mercury is very difficult.

\* The best, in such cases, consists in transforming the metallic sulphurets into metallic chlorides, and chlorides of sulphur, by means of gaseous chlorine, after which, the perchloride of mercury may be volatilised by heat from the non-volatile metallic chlorides.

\* This experiment is performed as follows:—The metallic sulphurets obtained are collected on a weighed filter, and washed rapidly, carefully dried at a gentle heat, and weighed. It is better still not to heat the sulphurets at first, but to desiccate them with the filter over sulphuric acid in vacuo. When perfectly dry, they are to be very gently warmed, in order to weigh them. The oxydisation of a small portion of the sulphurets is thus prevented, which otherwise cannot be avoided when the moist metallic sulphurets are dried in contact with the air.

\* Having taken a sufficient quantity of the dry sulphurets, it is introduced into a small glass bulb, which must be scrupulously cleaned with a feather. The bulb is first weighed whilst empty, and again weighed after the introduction of the sulphurets, in order to know the exact quantity operated upon.

Chlorine is then disengaged from bottle *a*, which contains a mixture of chloride of sodium, and of peroxyde of manganese, upon which concentrated sulphuric acid, mixed with its own bulk of water, is gradually poured through a funnel, until a slow and regular stream of chlorine gas is established.



\* Instead of the safety funnel-tube *b*, an ordinary funnel-tube, with a long stem, may be employed, similar to that (page 128) ; the only precaution to be taken consists then in introducing a glass rod, which reaches only so far as the beginning of the stem, so that the sulphuric acid poured in can fall only drop by drop in the flask.

\* When the whole apparatus is full of chlorine, the metallic sulphurets are very moderately heated in the bulb *e* ; chloride of sulphur is at first disengaged, which flows into the bottle *k*, where it is decomposed by the water contained therein, with separation of sulphur. The metals combine also with the chlorine, and the perchloride of mercury, being volatile, may be completely eliminated by the heat alone, from the other non-volatile chlorides. At a short distance from the right angle of the glass tube, acicular crystals are deposited, which consist of metallic chloride, and which would soon obstruct a tube of a small diameter ; they must be driven by the flame of a small spirit-lamp, and the heat is removed from the bulb when it is perceived that the subliming of new crystals has ceased.

\* After the complete cooling of the bulb, the operator cuts with a file that portion of the glass tube which contains the crystalline sublimate, and this sublimate is washed down by a stream of

water into the bottle *k*, when it dissolves in the water contained therein. The bottle is then closed by a glass stopper, and left in a moderately warm place, and after complete cooling, the undissolved sulphur is separated by filtering. When the disengagement of chlorine gas has been continued for a very long time, it sometimes happens that all the sulphur is dissolved, and converted into sulphuric acid. The liquor filtered from the sulphur is heated in contact with the air so long as it retains an odour of sulphur, and as soon as it has become inodorous, the operator proceeds to precipitate the sulphur by one of the methods mentioned before.

\* The bulb *e* contains the non-volatile chlorides. Generally, the quantity of the metal contained in them may be calculated from their weight, when, after the experiment, the bulb is rapidly weighed. The chloride is dissolved in water, and the bulb, after being dried, is weighed.

\* The oxydes of silver, of lead, and of copper, may likewise be separated from peroxyde of mercury in this manner, when the solution has been precipitated by sulphuretted hydrogen, which method is especially to be preferred to that by sulphuric acid, when the object is to separate protoxyde of lead from peroxyde of mercury. After having precipitated the oxydes from the solution by sulphuretted hydrogen, it is not necessary to dry the sulphurets obtained in vacuo; the drying may be performed in the open air, because the sulphurets of lead, and of mercury, are less easily oxydised in contact of the air than the other sulphurets. When sulphuret of lead is decomposed by gaseous chlorine, the operator must take care that the bulb be only very gently heated, for too high a temperature might volatilise a little chloride of lead, along with the perchloride of mercury. From the weight of the chloride of lead obtained, that of the oxyde of lead may be calculated more accurately than in any other way.<sup>1</sup>

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<sup>1</sup> Cyanide of potassium may be employed for separating mercury from lead; an excess of cyanide of potassium is to be poured in the solution of the two metals; an insoluble precipitate is formed, which contains all the lead, whilst the whole of the mercury remains in the solution, from which it may be precipitated as sulphuret of mercury.—Ed.

\* When this method has been employed for separating protoxyde of copper, and peroxyde of mercury, from each other, the quantity of the first of these peroxydes cannot be calculated from the weight of the chloride of copper contained in the bulb *c*, because it is a mixture of subchloride, and of protochloride of mercury, in various or indefinite proportions. The stronger has been the heat employed for heating the bulb, the larger the quantity of subchloride of copper in the bulb is. The bulb is therefore plunged in water containing nitric acid, which dissolves all the contents; and by pouring a solution of potash in the liquor thus obtained, the whole of the copper is precipitated in the state of protoxyde of copper.<sup>1</sup>

\* The oxydes of iron and of bismuth cannot be separated from peroxyde of mercury by this method, because the chlorides of these two metals are volatile.

QUANTITATIVE DETERMINATION OF PEROXYDE AND OF SUB-OXYDE OF MERCURY, WHEN THESE TWO OXYDES EXIST SIMULTANEOUSLY.

If a solution contains peroxyde and suboxyde of mercury simultaneously, and the operator has to estimate the relative proportions of these two oxydes, the liquor should first be diluted with a large quantity of water, especially if it be acid, and muriatic acid is then added thereto, which precipitates the suboxyde of mercury in the state of subchloride of mercury. This salt is collected on a weighed filter, and dried at an extremely gentle heat, until it no longer loses weight; it is then weighed, and from the weight observed, the quantity of the suboxyde of

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<sup>1</sup> Mercury can also be separated from copper by means of cyanide of potassium, in the manner which has been described for separating silver and cadmium from copper; but the following method by Bonsdorff is exceedingly convenient. If the mercury exists in the solution in the state of suboxyde, the operator begins by converting it into peroxyde by means of nitric acid; muriatic acid is then added to the solution of the two oxydes, and the solution of potash is poured in; if a solution of formiate of alkali is now added, the mercury will be precipitated in the state of subchloride of mercury, which is to be separated by filtering, and the copper in the filtrate is next precipitated by solution of potash.—ED.



mercury is calculated. Take now the liquor filtered from the precipitate, the peroxyde of mercury which it contains is precipitated by one of the methods which have been described, and the mercury obtained serves to calculate the quantity of the peroxyde of mercury contained in the solution.

\* In precipitating the subchloride of mercury, the operator must not omit to add a very large quantity of water to the liquor, especially if it contains nitric acid, because otherwise a small quantity of subchloride of mercury might be converted into perchloride. It is likewise necessary to take care not to filter immediately the subchloride of mercury produced, but to wait some time before beginning to filter. But all application of heat must be sedulously avoided, because the muriatic acid would be sufficient to convert the subchloride into perchloride of mercury, which is accompanied by the liberation of a certain quantity of metallic mercury.

\* If the substance which contains suboxyde and peroxyde of mercury is insoluble in water, it should be treated in the cold by very dilute muriatic acid, which in most cases leaves the suboxyde of mercury in the state of subchloride of mercury, insoluble, whilst it dissolves the peroxyde in the state of perchloride of mercury. The mercury in solution is afterwards reduced. When, on the contrary, the substance insoluble in water contains nitric acid, it is advisable to begin by dissolving it in dilute nitric acid, and then to add muriatic acid to the solution. If this acid, even diluted, were put in contact with the insoluble substance containing nitric acid, it might happen that a little subchloride of mercury would be converted into perchloride of mercury, and dissolved.

## CHAPTER XXVI.

## RHODIUM.

## DETERMINATION OF RHODIUM.

WHEN rhodium exists in a solution in the state of oxyde or of chloride of rhodium, the best method of determining it consists, according to Berzelius, in pouring an excess of a solution of *carbonate of soda* in the liquor, evaporating it to dryness, and igniting the dry residuum in a platinum crucible. After saturating it by water, peroxyde of rhodium remains, which is collected on a filter and washed, first with muriatic acid, and then with water; it is then calcined along with the filter, and treated by hydrogen gas, which reduces it easily. The metal thus obtained is weighed. This reduction by means of hydrogen gas may be effected in the same manner as that of oxyde of cobalt, which was described page 128. It is so much the more easily accomplished, that scarcely any heat is required.

It is difficult to separate rhodium from the other metals with which it may be mixed in solutions, because sulphuretted hydrogen gas precipitates it for the most part, but yet not completely. There are few substances, amongst those which have been hitherto treated of, with which it is found combined in the native state; wherefore it is not necessary to indicate here the means by which it could be separated from such substances. Rhodium exists only in the ores of platinum, and we shall see farther on, when speaking of platinum, how the metals contained in these ores can be separated.

## SEPARATION OF RHODIUM FROM SEVERAL OTHER METALS.

Rhodium, in the metallic state, being insoluble, even in aqua regia, might be separated from the other metals by means of the simple acids, yet its alloys contain it very often in such a state that these simple acids may frequently dissolve it along with the other metals, and at other times it prevents these metals from dissolving completely.

According to Berzelius, it may be easily dissolved by fusing it with *bisulphate of potash*. Rhodium dissolves in this salt at a red heat, under disengagement of sulphurous acid; but this solution is slowly effected, and requires that the operator should take care, whilst it is taking place, to close it with a tight cover, in order to retard the volatilisation of the excess of acid. As soon as, by removing the cover, the saline mass sets and crystallises at the surface, the crucible is withdrawn from the fire, and suffered to cool; the salt is then dissolved by boiling water, and the portion which resists solution is treated by a fresh quantity of bisulphate of potash. When the fused salt contains but little rhodium, it is red and transparent, but when it is nearly saturated, it has a dark or a black tinge. After cooling, it is either deep or light yellow, according to the quantity of the metal which it contains. Cold water dissolves it slowly, but it is easily soluble in boiling water. The solution is yellow.

So long as the salt continues to acquire a colour, it must be fused again. In order to avoid employing a considerable quantity of bisulphate of potash, the analyst may, when this salt appears to have lost the greatest part of its free acid, add weighed quantities of distilled sulphuric acid, and heat the whole cautiously, until the water of the acid will have dissipated, and then continue the fusion. That which remains insoluble must be treated in the same manner, so long as the salt receives a colour. When this ceases to take place, it is a proof that the salt does not take up any particle of rhodium.

Thus can rhodium be separated from the metals which are combined with it, and which are not attacked by bisulphate of potash.

#### SEPARATION OF RHODIUM FROM COPPER.

When a solution contains rhodium and copper, these two metals, according to Berzelius, can be separated from each other in the following manner:—The liquor is poured into a flask provided with a glass stopper, and sulphuretted hydrogen is passed through it, to complete saturation. The flask is then closed, and left at rest for twelve hours in a warm place. At the end of that time, both the sulphuret of copper and the sulphuret of rhodium have fallen down, the first completely, the second nearly so. The liquor is filtered, heated, and evaporated, by which means it again yields a portion of sulphuret of rhodium, which is added to the other metallic sulphurets already obtained. They are then roasted whilst still moist, in a platinum crucible, until sulphurous acid is no longer disengaged. The roasting being finished, concentrated muriatic acid is poured upon the mass; the acid assumes a green colour, because it holds a portion of basic sulphate of copper in solution, whilst peroxyde of rhodium is left behind. A solution of potash is poured in the liquor, in order to precipitate the protoxyde of copper.

The liquor filtered from the metallic sulphurets contains still a little rhodium, which may be obtained by freeing it first from sulphuretted hydrogen by heating it, and then treating it by carbonate of soda in the manner indicated before. The peroxyde of rhodium obtained, is to be reduced by hydrogen gas, and the metallic rhodium is then weighed.

#### SEPARATION OF RHODIUM FROM IRON.

Rhodium is met with in analytical research, combined not only with copper, but also with iron, since it has been employed latterly in small quantity, to alloy it with steel. According to Berzelius, it may be separated from iron in the following

manner:—A current of sulphuretted hydrogen is to be passed through the acid solution, in order to precipitate most of the rhodium in the state of sulphuret of rhodium, which is roasted, and then converted into peroxyde of rhodium. The liquor filtered from the latter is mixed, and heated with nitric acid, by which the protoxyde of iron is converted into peroxyde, which is precipitated by ammonia, washed, ignited, and weighed. The peroxyde of iron obtained, contains still some rhodium, and in such a state, that it is dissolved along with the peroxyde of iron by muriatic acid. The peroxyde of iron is reduced by hydrogen, and the metal is then dissolved by muriatic acid, heat being applied towards the end. The small portion of rhodium remains in a state which is not yet known, yet it is converted into peroxyde of rhodium by igniting it in the air. Its weight is deduced from that of the peroxyde of iron, from which the quantity of the iron is calculated.

The liquor from which peroxyde of iron was precipitated by ammonia, contains still a little rhodium, which may be separated by adding a sufficient quantity of carbonate of soda to the solution, evaporating to dryness, igniting the residuum, and treating it by hot water, peroxyde of rhodium remains insoluble. The various portions of peroxyde of rhodium are put together, and reduced by hydrogen gas.

#### SEPARATION OF RHODIUM FROM THE METALS OF THE ALKALIES.

When rhodium is combined in the state of perchloride of rhodium with chlorides of alkalies, and the operator wishes to separate them from the metals of the latter salts, it may be done, according to Berzelius, in the following manner:—Take a given weight of the metallic chlorides, and introduce it in an apparatus similar to that represented (page 128), and heat it in a current of hydrogen gas until the perchloride of rhodium is reduced under disengagement of muriatic acid gas, which is known when, by holding a glass rod, moistened with ammonia, at the extremity of the apparatus, white clouds cease to appear.

The glass bulb containing the salt under examination is weighed; the contents are now treated by water, which dissolves the salt, and leaves the reduced rhodium, which is separated by filtering; it is then dried, ignited in a current of hydrogen gas, and weighed. The filtered liquor which holds the chloride of alkali in solution is evaporated to dryness, the residuum is ignited and weighed.

## CHAPTER XXVII.

## PALLADIUM.

## DETERMINATION OF PALLADIUM.

THE best method of precipitating palladium from its solution, in which it ordinarily exists in the state of protonitrate or protochloride of palladium, consists, according to Wollaston, in treating it by a solution of *cyanide of mercury*. If the liquor contains only a small portion of palladium, the precipitate produced by cyanide of mercury does not appear immediately, the liquor becomes turbid only after some time, and yields a light-yellow precipitate, which becomes greyish-yellow when dry. This precipitate is ignited, and metallic palladium remains, the quantity of which may then be determined. The palladium becomes blue during ignition, but its weight is not thereby augmented in an appreciable manner. In this experiment it is necessary, if the solution be acid, to neutralise it by carbonate of soda.

\* When palladium has to be precipitated by cyanide of mercury from a solution which contains alcohol, it is necessary first to ascertain that the liquor contains no other metals, for the solution of cyanide of mercury determines in that of some other metals, for example, in solutions of platinum, of gold, &c., when they contain alcohol, and are left in contact with it for a long time and with the help of heat, precipitates which resemble that of cyanide of palladium, for which they might be mistaken.

## SEPARATION OF PALLADIUM FROM IRON AND OTHER METALS.

Palladium may be precipitated from its acid solutions by sulphuretted hydrogen, by which means it may therefore be easily separated from iron and other metals which are not precipitated from their acid solutions by this gas. The sulphuret of palladium thus produced is converted by roasting into basic sulphate of palladium, and then dissolved in muriatic acid. This solution is neutralised by soda, and by pouring a solution of cyanide of mercury into it the palladium is precipitated in the state of cyanide of palladium which may then be ignited.

## SEPARATION OF PALLADIUM FROM COPPER.

Palladium may, by means of sulphuretted hydrogen, but more especially by cyanide of mercury, be separated from nearly all the metals which may exist in solution with it, except copper, with which it is met with in impure platinum, and from which it may be freed, according to Berzelius, in the following manner:—The two metals are first precipitated in the state of sulphurets by passing a current of sulphuretted hydrogen through the acid solution; the sulphurets thus produced are washed whilst still moist, together with the filter, until sulphurous acid is no longer disengaged. They are thus converted into basic sulphates of copper and of palladium, which are dissolved in muriatic acid. The solution is mixed with chloride of potassium and nitric acid, and evaporated to dryness. A saline mass is thus obtained of a deep colour, which consists of chloride of potassium, potassio-chloride of copper, and potassio-chloride of palladium. The two first of these salts are separated by means of alcohol, sp. gr. 0·833, and the salt of palladium, which is insoluble in this menstruum, remains alone. It is collected upon a weighed filter and washed with alcohol; it is then washed and dried. It contains 28·84 per cent. of palladium. The quantity of palladium may also be determined by dissolving the saline mass in boiling water, and precipitating by cyanide of



mercury; but this method is more complicated, yet it deserves the preference, when the quantity of chloride of potassium to be separated by alcohol is too considerable.

The spirituous solution of the copper salt contains a trace of palladium, which, however, may be neglected. This liquor is evaporated to volatilise the alcohol, and the saline mass is dissolved in water, from which the oxyde of copper may be afterwards precipitated by solution of potash, and the quantity determined.

\* According to Döbereiner, copper may likewise be separated from palladium, by adding to the nitric acid solutions of the two metals properly diluted, a solution of formiate of alkali, and boiling the whole until the disengagement of carbonic acid has ceased. The protoxyde of palladium is reduced, and the metal may be collected in the state of a grey powder, or often also of shining spangles, whilst the protoxyde of copper remains in solution.

#### SEPARATION OF PALLADIUM FROM SILVER.

If the two metals are contained in a nitric acid solution, the silver may be precipitated in the state of chloride by means of muriatic acid.

#### SEPARATION OF PALLADIUM FROM THE METALS OF THE ALKALIES.

If palladium is combined in the state of chloride with chlorides of alkalies, from which it has to be quantitatively determined, the operation is the same as for separating chloride of rhodium from the chlorides of alkalies (page 319). Yet palladium may be ignited in the air, and does not require that the operation should be performed in an atmosphere of hydrogen gas.

## CHAPTER XXVIII

## IRIDIUM.

## DETERMINATION OF IRIDIUM.

THE following process may be resorted to for precipitating iridium from its solutions, and at the same time for separating it from nearly all the other metallic oxydes of which we have spoken before. The solution is first concentrated and a concentrated solution of *chloride of potassium* or of *sal ammoniac* is next added, after which very strong alcohol is poured into it, so that it may contain about sixty per cent. of its volume of alcohol. A precipitate of potash-chloride or ammonia-chloride of rhodium is thus produced, insoluble in alcohol, but which is completely soluble when the liquor contains a slight excess of chloride of potassium or of sal ammoniac. The precipitate is washed with spirits of wine. If the operator wishes to determine the quantity of iridium in the double salt which has formed, and if the latter has been precipitated by chloride of potassium, it is treated by hydrogen gas, in the same manner as for the potash-chloride of rhodium (page 219). When the double salt has been precipitated by sal ammoniac, the reduction immediately leaves the iridium in the metallic state, the quantity of which may then be determined. Sal ammoniac and muriatic acid gas are disengaged during the experiment.

I shall describe other methods of separating iridium when I come to speak of the means of isolating this metal from osmium and platinum.

## SEPARATION OF IRIDIUM FROM OTHER METALS.

Iridium may be completely separated by sulphuretted hydrogen from its acid solutions. Sulphurets of the metal are thus produced, the degrees of sulphuration of which correspond to the degrees of oxydisement of the metal in the liquor. These sulphurets are of a brown colour, or almost black, and they perfectly resemble those which are produced by platinum, palladium, and rhodium. They do not become acid by drying. By means of sulphuretted hydrogen iridium is easily separated from the substances which this reagent does not precipitate from an acid solution. The sulphuret of iridium produced dissolves in nitric acid, in the cold, without residuum, and when the solution is concentrated it may be separated therefrom by adding muriatic acid, chloride of potassium, or sal ammoniac and alcohol.

As sulphuret of iridium is soluble also in hydrosulphuret of ammonia, this reagent might likewise be employed for separating iridium from several metallic oxydes the sulphurets of which are insoluble therein. The sulphuret of iridium precipitated from such a solution by an acid is, according to Berzelius, soluble to a certain extent in water, to which it communicates a reddish-brown colour, so that after filtering the liquor, the water used for washing becomes strongly coloured. Yet a large excess of acid impedes the solubility of iridium, wherefore, when the liquor is evaporated, the dissolved portion separates by degrees, as the acid becomes gradually more concentrated, though the whole is not thus precipitated. A small quantity of nitric acid in the liquor subsequently oxydises the sulphuret of iridium whilst the liquor is evaporating, and transforms it into sulphate of iridium.

## CHAPTER XXIX.

## OSMIUM.



## DETERMINATION OF OSMIUM.

THE quantitative determination of osmium presents many difficulties, on account of the volatility of osmic acid.

If the combination under examination contains metallic osmium, and if this combination is susceptible of being completely dissolved by aqua regia, the solution is then to be performed in a glass retort, furnished with a receiver. The acid being then distilled, taking care to cool the receiver, the whole of the osmium is found in the product contained in the receiver.

The quantity of the osmium in this product may be ascertained in various ways. If the quantity thereof is very small, the best is, according to Berzelius, to dilute the distilled liquor with water, and to saturate it with ammonia, or with another alkali, so that the acid predominates a little. The liquor is then poured in a flask susceptible of being closed, and of such a capacity as to be almost filled by the liquor. A current of sulphuretted hydrogen gas is then passed through it to supersaturation. The flask is then to be closed, and left at rest until all the sulphuret of osmium shall have settled, which requires several days. The clear liquid is then decanted, or removed by means of a syphon or of a pipette, the sulphuret is placed upon a weighed filter, washed, dried, and weighed. It contains less osmium than should rigorously be, because it retains a little moisture, and is

slightly oxydised in drying. The quantity of osmium is about 50 or 52 per cent.

But when the quantity of osmium in a liquor is considerable, the best, according to Berzelius, is to precipitate it by mercury, previously adding to the solution a sufficient quantity of muriatic acid to enable the mercury to combine with the chlorine. A precipitate is thereby produced, which consists of subchloride of mercury, of a pulverulent amalgam of mercury, and of osmium, and of mercury containing very little osmium. The whole is heated in a glass bulb, on each side of which a glass tube is soldered, and a current of hydrogen gas is passed upon it. Fumes of the metallic mercury, and of the subchloride of mercury, escape with the hydrogen gas, whilst the osmium remains behind in the state of a porous, black powder, which has not a metallic appearance, but which acquires it by compression, or friction. The weight of this powder is then determined.

The liquor filtered from the precipitate contains osmium still, which may be precipitated by digesting it for a long time with mercury; but the experiment is very slow. It is, therefore, better to saturate the acid with ammonia, evaporate the liquor to dryness, and heat the remaining mass in a retort. Under the influence of heat, the ammonia decomposes the salt of osmium, and the mercury, if any, volatilises with the muriate of ammonia in the state of a double salt.

\* According to Döbereiner, formic acid is the best reagent for separating osmium from its solutions, even from that of osmic acid in potash; the metal precipitates under the form of a deep blue powder.

#### SEPARATION OF OSMIUM FROM OTHER METALS, AND PRINCIPALLY FROM IRIDIUM.

Osmic acid, being volatile, may, on that account, be easily separated from the other metals which may accompany it, except iridium, because it forms with this metal a particular

alloy, which is found in nature. In one of these alloys, which has a light colour, the two metals are united with a wonderful degree of intimacy. However repeatedly the operator may heat them in contact with the air, the osmium is not thereby converted into osmic acid, so that it cannot be recognised by the characteristic odour of the latter substance.

The best method of performing the extremely difficult analysis of this compound, is that proposed by Berzelius. The substance is first pulverised. It forms more or less bulky grains, which are solid, and very hard. They cannot be broken in a stone mortar, because they cannot be struck hard enough therein. It is best to use a steel mortar, or a steel ring with a steel plate. The grains are so hard, that when the blows are strong enough, they sink into the steel, in which they are held fast. They are thus broken as well as possible, and they are subsequently reduced into a powder which must be fine enough to rub between the fingers like plumbago. After having broken the pieces, they are pretty easily pulverised, and the operator must not spare any trouble to triturate well, because the fine powder is promptly decomposed, whilst a coarser powder is but slightly attacked.

This powder is boiled with muriatic acid, which dissolves with effervescence the iron abraded from the tools, the solution of iron is decanted, and the powder left behind is well washed, after which, it must be mixed with somewhat less than its own weight of nitrate of potash recently fused, and, consequently, free from water. The mixture is introduced into a small porcelain retort, furnished with a tubulated receiver, from which a disengagement tube issues, which plunges into a vessel containing dilute ammonia. The retort is heated at first very slowly, and taking care that the disengagement of the gas does not proceed too violently, because the mass might otherwise be projected from the retort. The heat is increased towards the end up to a full white heat; when gases are no longer disengaged, the retort is suffered to cool.

The contents of the retort are then treated by cold water,

and the solution thus obtained is put in a glass stoppered flask, into which it is mixed with a large proportion of muriatic and of nitric acid, so that it should be strongly acid. It then exhales a strong odour of osmium. The clear portion of this liquor is introduced in a retort, and distilled, taking care to lute the joints well, and to keep the receiver constantly cool. The undissolved portion is likewise mixed with the muriatic and nitric acids, and distilled in a separate retort. The product contains osmium also, and that which remains in the retort is iridium, with a small quantity of osmium.

The clear liquor must be separated from the portion which has not dissolved, in order to avoid spirting in boiling it, which might cause a little of the solution of iridium to penetrate into the receiver. The alkaline solution must not be filtered through paper, because this substance would partially deoxydise it, and the paper would then be coloured green by protoxyde of iridium, and the liquor would pass through it with extreme difficulty. The nitric acid is put in excess, in order to destroy the double chlorides of osmium, and to convert this metal into volatile osmic acid.

That which remains in the two retorts after distillation is filtered, mixed with chloride of potassium, and dried, to eliminate the excess of the muriatic and nitric acids. The dry saline mass is carefully mixed with carbonate of soda, and the whole is heated in a retort in the same manner as before, and the oxyde of osmium which is disengaged is collected; the salt is then dissolved in water, which leaves the peroxyde of iridium behind. Sometimes it contains a little rhodium, which is subsequently separated by fusion with bisulphate of potash, following the course which has been described above (page 217).

After all these operations the iridium still retains a certain quantity of osmium, which adheres to it with extraordinary firmness. It may be separated from it by reducing the two metals by hydrogen gas at a very gentle heat, and keeping them at a low red heat in the air, until the odour of osmic acid is no longer perceived. In such case the iridium must be reduced

and oxydised several times, in order to free it from osmium, which result is, however, attained only with difficulty, and very slowly. When iridium is heated too strongly to a white heat, the two metals unite again, they shrink, and the osmium ceases to burn.

The weight of the iridium is determined, after reduction, with hydrogen gas. The osmium is separated from all the solutions which contain it, in the manner which has been described before. The small quantity of the metal, the oxyde of which has volatilised pending the ignition of the iridium, is ascertained from the difference which exists between the weight of the peroxyde of iridium, containing a little osmium, after the first reduction with hydrogen gas, and that of the same oxyde after the last ignition and last reduction with hydrogen gas.

In that which remains after the treatment of the ores of platinum by aqua regia, besides the shining and silvery crystalline spangles of osmiuret of iridium, which are met with in the platinum ores of the Ural mountains, there are, according to Berzelius, a multitude of small rounded grains of an uneven surface, which are less rich in osmium than the crystalline osmiuret of iridium. In analysing these grains, the operator finds that besides osmium and iridium, they contain several substances which exist, it is true, in the state of mixture only, and not as essential constituents, but which are mixed in such a manner, that they cannot be separated by mechanical means. They are, titanio acid, silicio acid, chromic acid, chromic oxyde, zirconia, and peroxyde of iron. Their presence is evidently referrible to chrome-iron, titanio iron, and hyacinths, which cannot be distinguished by the naked eye from the grains of the alloy of osmium and iridium, and which cannot be separated from it by levigation.

For the purpose of analysing these grains, Berzelius proposed a method which differs from that which we have just described. After fusing the mass with nitrate of potash, it is mixed with water, in order to dissolve all the saline substances. The mixture is poured in a tubulated retort, and left there until it has become



clear. The dissolved portion is decanted. The residuum is treated by a fresh quantity of water, which is again to be poured off when it has become clear. The decanted liquors contain sulphate, chromate, silicate, sesquioxide of iridium, and a little osmate of potash. By distilling them in a retort with muriatic acid the whole of the osmium contained therein is obtained. As to the means of determining quantitatively the other substances which exist in the solution, we shall speak of them farther on, when treating of these substances.

That which has remained undissolved in the tubulated retort is mixed with muriatic acid, which extracts all the soluble portions of this residuum. The liquor is then distilled by means of the water-bath, and the operation is continued until a small portion of the liquor, being withdrawn by the tubular of the retort, is found to possess no odour of osmium. The product of the distillation is a solution of osmic acid in water, which contains a little chlorine. The residuum in the retort being treated by a small quantity of water, yields a green liquor of a more or less deep hue, which colour is due to the presence of protochloride of chromium. When washing the undissolved residuum with weak alcohol, the whole of the protochloride of chromium may be removed, and potash-chloride of iridium remains on the filter. The green liquor and the spirituous liquid become both turbid, when, after diluting them with water, they are heated; a white powder is thus precipitated, which resembles titanac acid, but which contains at the same time silicic acid and zirconia.

\* The analysis of the alloy of osmium and iridium may be performed in a more exact manner by determining the osmium, not immediately, but from the loss sustained.

\* To effect this, Berzelius directs to proceed as follows:—The alloy of osmium and iridium is first reduced into fine powder in the manner described before; it is fused with hydrate of potash in a gold crucible, to which, however, one of silver may be substituted. The hydrate is added only by degrees to the

metallic powder. At first the operator only moistens the powder with it, but without covering it, by which means the oxydisation is much accelerated, provided the air be admitted as freely as possible. A little chlorate of potash may also be added; but the effervescence produced by the disengagement of the oxygen gas prevents the use of this reagent, when the analysis is required to be very accurate, though it considerably hastens the solution of the metallic powder. The heat must hardly exceed incipient redness; if the analyst operates upon about one *gramme* of powder, the heat must be prolonged for an hour and a-half, taking care to stir the mass, from time to time, with a small gold spatula.

\* Despite all these precautions, it often happens that the whole of the metallic powder is not oxydised, which is recognised by dissolving the fused mass in water. The undissolved portion is boiled with muriatic acid, and the blue oxyde of iridium undissolved is carefully separated from the metallic powder, the weight of which is deducted from the mass experimented upon. The alkaline liquor is supersaturated with muriatic acid, which produces a disengagement of osmic acid. A little nitric acid is further added, and the metal is evaporated to dryness in an open vessel. The saline mass is dissolved again in water, and carbonate of soda is added to the liquor, until it becomes feebly alkaline, which at first does not produce any apparent precipitate; the liquor is then evaporated to dryness, and the dry residuum is ignited. The saline mass is treated by water. If the solution emits, whilst being heated, an odour of osmic acid, it must be left to digest until that odour has disappeared. It is then filtered, and there remains on the filter an oxyde of iridium of a fine bluish-black colour which should be washed with a weak solution of sal ammoniac, because, if pure water were used to wash it, it would pass through the paper. The oxyde of iridium obtained, being treated by aqua regia, must be insoluble in this menstruum. If it contains platinum, it will dissolve in it, in which case chloride of potassium must be added, and the liquor evaporated. The

solution ordinarily contains peroxyde of iron, which is precipitated by ammonia, and which may be separated from a certain quantity of palladium, with which it is mixed, by means of cyanide of mercury.

\* The oxyde of iridium is reduced by hydrogen gas, the residuum is weighed, and repeatedly melted with bisulphate of potash, in order to separate the rhodium and palladium which might be mixed with it. The oxyde of iridium is next treated by hydrogen gas, and from the difference between the weight now, and in the preceding experiment, the quantity of the other metals is known. The oxyde of rhodium, which has dissolved, is treated as we have said, page 216. After having washed, ignited and weighed it, it is treated by aqua regia, which might dissolve a little palladium, which the operator would precipitate by means of cyanide of mercury.

\* By following this method, the quantity of osmium contained in the compound is known by the loss sustained.

\* In order to facilitate this troublesome decomposition of the native alloy of iridium and osmium in the residuum of platinum ores, Wöhler proposed the following method:—The residuum, which needs not be reduced into fine powder, is mixed with an equal weight of decrepitated and well-pulverised chloride of sodium. A long and large glass tube is filled with this mixture, and placed in a small combustion furnace similar to that used for the combustion of organic substances by protoxyde of copper, and a drawing of which will be represented farther on, when we come to treat of the decomposition of organic substances. One of the extremities of the tube is connected with an apparatus for the disengagement of chlorine, the other communicates with a small balloon, provided likewise with a disengagement tube, and which balloon serves to receive the volatilised osmic acid. The disengagement tube of the balloon plunges into a flask containing dilute ammonia, in which the portions of osmic acid which have escaped condensation are dissolved.

\* Ignited pieces of charcoal are now placed under the tube,

and through its whole length, so as to bring the mixture to a low red heat, after which the disengagement of chlorine gas is begun, and directly passed through the mass. The current must not be too rapid, nor does it need drying. The gas is absorbed so abundantly and so completely, that in the first instance no bubbles pass through the ammonia. When the bubbles begin to pass actively, which takes place in about two hours, if the mass in which the quantity of osmium and iridium has to be determined is large, the experiment is terminated; the apparatus is then suffered to cool, and is dismounted.

\* In this experiment soda-chloride of iridium and soda-chloride of osmium are formed, which are both soluble in water; the titanico-iron, chrome-iron, and other substances not being attacked, remain in solution. But the moisture of the gaseous chlorine appears to decompose the chloride of osmium in a continuous manner, in such a way that muriatic acid and osmic acid are formed whilst metallic osmium is separated, which is thus again exposed to the action of the gaseous chlorine. The operator likewise finds generally in the anterior part of the tube a certain quantity of chloride of osmium, of a deep green or red colour. One thing is certain; it is that the greatest part of the osmium is obtained in the state of osmic acid.

\* The metallic osmium is subsequently extracted from the osmic acid, from the chloride of osmium, and from the ammoniacal liquor, by following the course mentioned page 226.

\* The contents of the tube which have been treated by chlorine gas are slightly agglutinated, but by putting the whole tube in a cylinder full of water, the mass may be easily detached, and all that which is soluble is thus dissolved. The solution has a deep reddish-brown colour, and consists of the double salts of iridium. This liquor smells strongly of osmic acid, which is due to the decomposed chloride of osmium. The liquid portion is poured off, to separate it from the undissolved portion, which still contains large spangles of the alloy of osmium and iridium. The decanted liquid is subjected to distillation, in order to obtain the osmic acid which it contains,

and for which purpose the vapours are received in dilute ammonia. When about half the liquor has passed over, the distillation is suspended, and the liquor is filtered.

\* The liquid is then poured in a capsula and evaporated, an excess of carbonate of soda being gradually added during the evaporation, by which a precipitate, which at first is brown, but which by degrees becomes bluish-black as the boiling proceeds, is obtained. The dried mass, which is black, is slightly ignited, then, after cooling, treated by hot water; there remains a powder of a coal-black colour, which consists principally of sesquioxide of iridium (oxyde susirideux). This powder is washed and dried; the saline solution is thrown away, for it contains nothing else than chloride of sodium and carbonate of soda, mixed with a little chromate of alkali, which imparts a yellow colour to it.

\* The sesquioxide of iridium contains not only osmium, for the extraction of which a particular process is required, but peroxyde of iron also. It is introduced in a glass vessel, and a current of hydrogen is passed over it. Ordinarily it becomes red hot spontaneously, so that heat need not be applied externally. It is best, however, to heat the tube, and to keep the oxyde at a low red heat, exposed to the stream of hydrogen, so long as water is formed.

\* The metallic iridium thus obtained is a black powder; it contains much soda which was in a state of chemical combination with the sesquioxide of iridium, and which must be extracted by water. Muriatic acid is poured upon it, with which it is left to digest, and which oxydises the iron.

\* The residuum of platinum ores is not exhausted by one treatment; it must be mixed with half its weight of chloride of sodium, and submitted to the same operation a second time.

\* According to Döbereiner, the operator may, as had been indicated by Persoz before, decompose the alloy of osmium and iridium by igniting it with sulphuret of sodium in maximum of sulphuration the product being ignited with one part of

carbonate and two parts of nitrate of potash, is almost entirely oxydised, so that, by treating the mass by water first, and then by dilute nitric acid, and lastly by muriatic acid, there remains only an insignificant residuum of undecomposed osmiuret of iridium.

\* There is a more easy method of decomposing other varieties of the alloy of osmium and iridium which differ from the preceding alloy by their dark colour, but which are found associated with it. Besides their colour, these varieties have another peculiarity, which distinguishes them from the ordinary light-coloured alloy of osmium and iridium above mentioned; it is this, that they lose their metallic lustre by exposure to heat, and disengage a penetrating odour of osmic acid.

\* The analysis of this alloy being easy, very small quantities of a few centigrammes only may be taken, which precaution is so much the more necessary that each spangle of alloy may have a composition differing from the others.

\* The *modus operandi*, according to Berzelius, is as follows:—The alloy is to be roasted in a small counterpoised platinum crucible at a white heat. In the course of a quarter of an hour, its appearance is altered, and it has become covered with a layer of deutoxyde of iridium. The loss is afterwards very trifling, though it continues to take place. The roasting is accelerated by dipping a glass rod in rectified essential oil of turpentine, with which the interior of the red-hot crucible is moistened. The vapour of the oil not only reduces the iridium, but it combines with the carbon of the oil under a disengagement of light, after which, when the oil has volatilised, it again burns, emitting at the same time an odour of osmium. This operation is repeated until all further diminution of weight has ceased. The residuum is reduced by means of hydrogen, and thereby converted into metallic iridium.

## CHAPTER XXX.

## PLATINUM.

## DETERMINATION OF PLATINUM.

A GREAT number of substances possess the property of precipitating platinum from its solutions in the metallic state; but that which answers the purpose best is mercury, or the solution of subnitrate of mercury. The precipitated platinum contains mercury; it is washed, dried, then strongly ignited and weighed.

\* It is best, however, to treat the solutions of platinum like those of palladium (page 223), by a formiate of alkali.

The best method of determining platinum quantitatively from its solutions is the following:—The acid solution of this metal is first concentrated, and a very concentrated solution of sal ammoniac is then poured into it, taking care to add alcohol in sufficient quantity to induce the precipitation of the ammonia-chloride of platinum produced.<sup>1</sup> This salt is washed with weak alcohol, to which a little sal ammoniac has been added. It is not easy to determine the quantity of the platinum from the weight of this precipitate, because the latter may contain an excess of sal ammoniac. Wherefore it must be ignited, after which operation metallic platinum remains in a porous state, and its weight may then be determined.

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<sup>1</sup> Before adding the sal ammoniac, the solution, if acid, should be almost neutralised with ammonia, so that the free acid should remain in slight excess only. The ammonia-chloride of platinum produced, requires a long time to settle, and the liquor, after the addition of the alcohol, should therefore be left at rest for about twenty-four hours before proceeding to separate the precipitate by filtering.—Ed.

The operator must, however, proceed very carefully when calcining this salt for quantitative determination, because it may happen that the vapours which are disengaged would mechanically carry away a little platinum in a fine state of division. In order to avoid all loss, it is best not to follow the usual method of igniting precipitates, and which consists in shaking them from the filter into the platinum crucible; the salt is, on the contrary, wrapped up in a piece of paper, a moderate heat is applied for a long time in a crucible closed with its cover, the paper becomes thus carbonised, and when the heat becomes a little stronger, chlorine and muriate of ammonia are disengaged without mechanically driving off any portion either of undecomposed salt or of reduced platinum. The crucible is then half uncovered, and the charcoal of the filter is then consumed in the usual way, by increasing the heat. This process presents, it is true, a few additional difficulties and is a little longer than in the ordinary way of calcining precipitates, but this is well compensated, because all loss of platinum is thus perfectly avoided. The reduction of the salt may also be effected with hydrogen gas, by means of an apparatus similar to that employed for the reduction of chloride of rhodium (page 219). Chloride of ammonium and muriatic acid gas are disengaged, and metallic platinum remains.

*Chloride of potassium* precipitates platinum more completely still than muriate of ammonia. To the concentrated solution of platinum in aqua regia, a sufficient quantity of strong alcohol is added, so that the liquor may contain about sixty per cent. of its bulk of alcohol, after which a concentrated aqueous solution of chloride of potassium is poured in.<sup>1</sup> The precipitate produced is washed with spirits of wine, containing about sixty per cent. of its bulk of alcohol, and to which a small portion of concentrated aqueous solution of chloride of potassium has been added. This precipitate, when not considerable, must be ignited in the same manner as that produced by muriate of ammonia; it is

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<sup>1</sup> If the solution contains much free acid, it should be neutralized by potash before adding the chloride of potassium.—En.



thereby converted into a mixture of metallic platinum and chloride of potassium. The ignited mass is treated by water, which dissolves the chloride of potassium, and leaves the platinum; the latter is then ignited and weighed.

If the quantity of the precipitate is considerable, that is, if more considerable than a few decigrammes, it is better to effect the reduction by means of hydrogen gas, in an apparatus similar to that which is used for the reduction of the potassio-chloride of rhodium (page 219).

#### SEPARATION OF PLATINUM FROM SEVERAL OTHER METALS.

By properly treating the peroxyde, or, rather, the perchloride of platinum, by muriate of ammonia, or by chloride of potassium, platinum may be separated from a great number of metals in solution, especially from all those the chlorides of which are soluble in weak alcohol, such as manganese, iron, cobalt, copper, mercury, &c. Although a small portion of another metallic combination is precipitated along with the platinum compound, this small portion may be easily separated from the reduced platinum by digesting the latter, after ignition, in nitric or in muriatic acid, which acids are separately without action upon platinum. Thus, for example, if a little chloride of lead has fallen down with the platinum compound, it may be separated from the reduced platinum simply by water, or by digestion in muriatic acid if a portion has already been converted into protoxyde of lead.

\* When chloride of potassium has been employed to precipitate platinum and separate it from these metals, it should be washed in the manner described before, until hydrosulphuret of ammonia no longer produces a precipitate in the filtered liquor.

Sulphuretted hydrogen precipitates platinum from its acid solutions in the state of sulphuret, but the latter is very easily oxydised by exposure to the air.<sup>1</sup> This process might, however,

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<sup>1</sup> Sulphuret of platinum, by exposure to the air in a moist state, is gradually converted into sulphuric acid and metallic platinum; ignition reduces it altogether into metallic platinum.—ED.

be resorted to for the purpose of separating platinum from metallic oxides which are not susceptible of being precipitated from an acid solution by sulphuretted hydrogen.

When a solution of platinum is rendered neutral or alkaline by adding soda thereto, and an excess of hydrosulphuret of ammonia is poured in it, the sulphuret of platinum produced dissolves in an excess of the reagent.<sup>1</sup> This method might be employed to separate the metals the sulphurets of which are insoluble in an excess of hydrosulphuret of ammonia. Yet it is better in all cases to precipitate the platinum in the state of potash-chloride or ammonia-chloride of platinum,—and thus separate it from the other oxides in solution with it.

When, however, platinum is met with in the metallic state, combined with some of the other metals of which we have treated, the simplest analytical method would be to treat the compound by nitric acid, which would oxydise and dissolve all the metals without attacking the platinum. Yet, we should remark, that when platinum is combined with other metals, it very often happens that it dissolves in the nitric acid with the other metals. Thus, for example, platinum and silver cannot be separated from each other by nitric acid, because the former is partially dissolved by the acid along with the silver.

Sulphuric acid, however, may be employed to separate platinum from silver. If this acid be boiled with these two metals, it dissolves the silver only, with which it forms sulphate of silver, and leaves the platinum untouched. The separation of the two metals may also be obtained by treatment with aqua regia, and separating the silver in the state of chloride of silver, from the dissolved platinum.

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<sup>1</sup> Sulphuret of platinum is also soluble, at least partially so, in the caustic alkalis, but some platinum is at the same time separated.—En.

SEPARATION OF PLATINUM FROM OSMIUM, IRIDIUM, PALLADIUM,  
RHODIUM, COPPER, AND IRON.—ANALYSIS OF THE NATIVE  
ORES OF PLATINUM.

The separation of platinum and of the metals with which it is associated in its ores is beset with many and great difficulties, which it was reserved for Berzelius to conquer. The method prescribed by him for the analysis of the ores of platinum is the following :—

The operator first picks up the grains of the ore which differ from the others by their appearance, and examines whether any of them are capable of being attracted by the magnet. Besides the small spangles of native iron which Osann has detected in them, the platinum sand often contains combinations of iron and platinum, both in the metallic state, which not only are attracted by the magnet, but even possess polarity. These grains have a different composition from those which are not magnetic. They may be separated by the magnet, and their relative proportion is determined.

The sample is next treated by dilute muriatic acid. The object of this experiment is to remove the crust of peroxyde of iron which covers these grains, and to dissolve the metallic iron. This done, the quantity of the iron which has thus been found in the sample is determined.

The latter, that is the sample, must not be ignited without previously weighing it, for it ordinarily becomes covered during this operation with a pellicle of peroxyde of iron, which augments its weight. It is sufficient to dry it upon a hot sand-bath.

The plan of the analysis, properly so called, should vary according to the quantity and nature of the constituents of the platinum ore; but it remains the same for all the ores hitherto known, as well for those from Asia as those from America, because they all contain the same substances, but in somewhat different proportion only. These substances, enumerated in the order of their relative quantity, are platinum, iron, iridium,

copper, rhodium, palladium, and osmium. Iridium and osmium exist in the ores of platinum in two different states, either really alloyed with the other metals, or simply agglomerated in their mass under the form of small particles of osmiuret of iridium. In the first case they dissolve with the platinum; in the second case they remain insoluble under the form of small shining and bright spangles which are so delicate and light that they may be spread on the skin like plumbago. When larger grains of osmiuret of iridium are left undissolved, it is a proof that the operator has not carefully picked them out. It is sometimes important to determine their relative quantity, which is best done by dissolving the remainder of the ore.

The analyst must not operate upon so large a portion of the ore; five grammes are rather too much, and Berzelius directs two grammes as the most commodious quantity. Yet, when the object in view is to determine with the greatest accuracy the proportion of a substance which exists in the ore, in a very small proportion only, a larger quantity of the ore should be dissolved, and then all the other substances may be neglected except the one which is the object of a particular research.

Berzelius dissolves the weighed portion of the ore by means of aqua regia, in a small glass retort provided with a receiver, which must be kept cool. The acid which distils during the solution is yellow. This colour is not only owing to the presence of chlorine, but to some of the constituents of the solution which during the effervescence have been lifted up in the form of a thin cloud, and which the disengagement of nitric oxide gas prevents from falling back in the retort. Even spangles of osmium and iridium, which have thus been driven up, are sometimes found in the receiver. The acid is distilled until the liquor has acquired a syrupy consistence, and stiffens on cooling. The saline mass is dissolved in the smallest possible quantity of water, and the solution is very carefully decanted. The acid which has distilled over, is poured back upon the undissolved residuum, and it is redistilled; thus, that which had

resisted solution the first time, is ordinarily dissolved at the second operation. The liquor is likewise concentrated to syrupy consistence. When the product of the distillation is not colourless, it must be redistilled over; it generally contains osmic acid, a little of which is lost by redistilling, but the quantity thus lost is generally very trifling.

The colourless product is diluted with water, and saturated either with ammonia or with hydrate of lime, if it be found that the use of the volatile alkali is too costly; yet it is necessary that there should be a slight excess of acid.

The object of this saturation is to prevent the sulphuretted hydrogen gas employed subsequently to precipitate the liquor from being decomposed by the influence of the acids. The precipitation must be effected in a flask capable of being closed, and which must be almost filled with the liquor. As soon as this liquor is supersaturated with sulphuretted hydrogen, the flask is corked up and left at rest until it has become clear, which sometimes requires one or two days. The clear portion is removed with a syphon or with a pipette, and the sulphuret of osmium is collected upon a weighed filter; it is washed, dried, and weighed. Theoretically, the sulphuret of osmium thus obtained, should contain 60·6 per cent. of metal; but it cannot be obtained free from sulphur and moisture, and it becomes thus slightly oxydised in drying. After several trials upon weighed quantities, Berzelius found that the sulphuret resulting from the experiment just related, contains from 50 to 52 per cent. of osmium (page 227). But the quantities of osmium are ordinarily so trifling, that an error of a few hundredths in the calculation of the osmium contained in the preparation is of very little consequence.

With respect to the metallic solution, it sometimes happens that, after having dissolved the saline mass in water, the liquor exhales the odour of chlorine. This is owing to the decomposition of the chloride of palladium. The solution must then be digested until all odour of chlorine has disappeared. If the liquor should become turbid, it would be owing to a precipitation

of oxide of palladium, which must be redissolved. The solution is passed through a weighed filter, which retains the undissolved particles. This residue consists in grains of osmiuret of iridium, in sponges of the same combination of which we have spoken above, in grains of sand, &c., which could not be picked out at the beginning. Sometimes a black powder is also obtained similar to charcoal, and which has a tendency to traverse the filter during the washing. It consists of peroxide of iridium, and is produced principally when the aqua regia contains too much nitric acid; for when the saline solution becomes concentrated, the iridium is oxydised at the expense of the latter acid, and chlorine is disengaged; hence an inconvenience, which it is difficult to avoid, namely, that the iridium cannot be separated from the osmiuret of iridium, because both are insoluble in all liquids, consequently the operator must, from the beginning, use all the necessary precautions to prevent this effect.

The filtered solution is mixed with double its bulk of alcohol of sp. gr. 0.833; the mixture will then contain 60 per cent. of its bulk of alcohol. A concentrated aqueous solution of chloride of potassium is added, until it ceases to reproduce a precipitate. The precipitate consists of potash-chloride of platinum, and potash-chloride of iridium, containing a little potash-chloride of rhodium, and a little potash-chloride of palladium, all of which are precipitated nearly in the same manner, and all the crystals further contain a little of the mother water. The precipitate has a fine lemon-yellow colour when it contains no iridium; in the contrary case, it may have all the various tints of red from deep orange-yellow to cinnabar-red. It is collected on a filter, and washed with spirit of wine, containing 60 per cent. of alcohol, to which a small quantity of concentrated solution of chloride of potassium has been added. The washing is continued until the filtering liquor ceases to be precipitated by sulphuretted hydrogen.

The analytical operations are then divided into two parts:

A, treatment of the washed precipitate;

B, treatment of the alcoholic liquor.

## A. TREATMENT OF THE WASHED PRECIPITATE.

The double salt, after having been washed, is dried, and very accurately mixed with its own weight of carbonate of soda. The filter is burnt with the portion which cannot be detached from it, and after mixing the ashes thereof with a little carbonate of soda, it is added to the rest. The whole is put in a porcelain crucible, and very gently heated until the mass has become black throughout. If this operation were performed in a platinum crucible, there would be danger, and this may very easily take place, that under the influence of the alkali, some protochloride of platinum may be produced at the expense of the crucible, and mixed with the perchloride of platinum, which would cause an unexpected excess in the analytical result.

Under this treatment, the double salts of the alkali are decomposed, and the platinum, the oxygen of which is carried away with the carbonic acid, is reduced, whilst the rhodium and the iridium remain oxydised, and in a state which permits the separation of the platinum from them by solution. When, instead of chloride of potassium, muriate of ammonia is employed, which is often the case, to precipitate the platinum, it often happens that in heating the precipitate in a crucible, the rhodium and iridium are reduced at the same time as the platinum, and that they are subsequently redissolved, when the whole comes to be treated by aqua regia.

The heated saline mass is washed with water. When the greater part of the salt has thus been removed, dilute muriatic acid is added for the purpose of extracting the alkali contained in the oxydes of iridium, and of rhodium, after which, these oxydes are washed, dried and ignited. The filter may be burnt, and the ashes deducted; but care must be taken to burn the filter by itself, in order to prevent the reduction of the oxydes by the combustible gases which are disengaged from the paper. The mass is then weighed.

This being done, the mass must be mixed with five or six times its weight of bisulphate of potash, and fused in a platinum

crucible, in the manner indicated in speaking of rhodium, (page 217). This operation is repeated several times in succession, until the flux ceases to acquire a colour.

The quantity of the rhodium may be determined in two different ways. The undissolved platinum is washed, ignited, and weighed; the loss indicates the quantity of rhodium which has dissolved, and which contains 71 per cent. of metallic rhodium; or else the solution of the acid salt, which contains the rhodium, is mixed with an excess of carbonate of soda; the liquor is exsiccated, and the salt which is left is ignited in a platinum crucible. After dissolving this salt in water, the oxyde of rhodium remains; it is collected on a filter, washed, burnt with the filter, and reduced by hydrogen gas. The metal thus obtained is weighed. It is best to employ the two methods. The rhodium obtained in this manner sometimes contains palladium, which latter metal is extracted by aqua regia, and after neutralising the solution, it is precipitated by cyanide of mercury. The weight of the palladium obtained is deducted from that of the rhodium.

After having extracted the rhodium, the metallic mass is treated by very dilute aqua regia, with which it is left to digest, in order to remove the pure platinum. The solution has a very dark colour, owing to some oxyde of iridium held in suspension, but when it has become clear, its colour is pure yellow. It is then to be decanted, and concentrated aqua regia, to which chloride of sodium has been added, is poured on the residuum, and the liquor is evaporated to dryness. The object of this addition of chloride of sodium is to prevent the production of protochloride of platinum. A little iridium dissolves in this more concentrated acid, but if concentrated acid were not used, a notable quantity of platinum would remain in the iridium. Upon this dry mass being dissolved, the oxyde of iridium remains behind. When it is washed with pure water, it almost always passes through the filter; wherefore, in order to separate it from the solution of platinum, the operator should always wash it with a weak solution of chloride of sodium, and then, in order



to expel the latter, it must be washed with a weak solution of muriate of ammonia, the last traces of which are to be finally expelled by ignition. The washed residuum is burnt with the filter, reduced by means of hydrogen gas, and weighed. The solution of the soda-salt containing iridium is mixed with carbonate of soda, dried, and ignited. A mixture of platinum and of peroxyde of iridium is thus obtained, which is purified from the salt by washing, and after treatment with aqua regia, the peroxyde of iridium remains behind. Ammonia still precipitates from the solution a trace of brown peroxyde of iridium, which, however, is not completely free from platinum. The peroxyde of iridium is reduced, and the quantity of the metal is added to that already obtained before. In order now to obtain the weight of the platinum, that of the peroxyde of rhodium must be deducted from the joint weight of the platinum and of the oxydes of rhodium and of iridium. To the weight of the metallic iridium obtained, the operator must add 12 per cent. of its weight, in order to obtain that of the peroxyde of iridium, which is to be further deducted from the weight of the platinum. The reduction of the platinum from its solutions, and the determination of its weight, would only lengthen the process, without rendering the result more accurate.

#### B. TREATMENT OF THE ALCOHOLIC LIQUOR.

This liquor is poured in a glass-stoppered flask, and sulphuretted hydrogen is passed through it to perfect saturation. The flask is then closed, and left at rest for twelve hours in a warm place. At the end of this time all the metallic sulphurets are precipitated. Sometimes the liquor has a red colour, which is due either to rhodium or to perchloride of iridium. The liquor is filtered, and the alcohol thereof is evaporated, during which operation a further precipitation of metallic sulphuret takes place, which must be added to those already produced. This mixture of sulphurets consists of sulphurets of iridium, of rhodium, of palladium, and of copper, whilst the

liquor retains iron, a little iridium and rhodium, and a trace of manganese. Pending the evaporation of the alcohol, a deposit of a metallic sulphuret, of a greasy nature, and of a fetid smell, takes place in the vessel, which cannot be removed by washing. After having suffered the solution to drain well, a little ammonia is added in the capsula containing this substance, by which it is dissolved. This solution is put in a platinum crucible, and evaporated to dryness. The metallic sulphurets, still moist, are placed upon the residuum, and the whole is roasted in the crucible until sulphurous acid ceases to be evolved. The roasting being terminated, concentrated muriatic acid is poured upon the mass, which assumes a green, or yellowish-green colour, because a basic sulphate of protoxyde of copper, and a basic sulphate of peroxyde of palladium are dissolved. The oxyde of rhodium, peroxyde of iridium, and a little platinum remain undissolved.

The muriatic acid solution is mixed with chloride of potassium and nitric acid, and evaporated to dryness. A dark-coloured saline mass is thus obtained, which consists of chloride of potassium, potash-chloride of copper, and potash-chloride of palladium. The two first of these salts dissolve in alcohol of sp. gr. 0.833, and may thus be removed, but the palladium-salt being insoluble in this menstruum, is collected on a counterpoised filter, and washed with alcohol. It contains 28.84 per cent. of palladium. The saline mass may likewise be dissolved in boiling water, and the solution precipitated by cyanide of mercury, for the purpose of thus determining the palladium which it contains, but this method is more complicated; yet it should be preferred when the quantity of the chloride of potassium to be extracted by the alcohol is too considerable.

The alcoholic solution of the salt of copper contains a trace of palladium, which, however, may be altogether neglected. This solution is evaporated in order to eliminate the alcohol, and the copper is precipitated either by a solution of pure potash, or by means of a rod of iron, after previously adding sulphuric acid. If the palladium has to be extracted from this

copper, it should be dissolved in nitric acid; the solution is neutralised and mixed with cyanide of mercury, which sometimes produces a very slight precipitate of cyanide of palladium containing copper, which is to be collected on a filter, burnt along with the filter, and the weight of which must be determined. Ordinarily the quantity is so inconsiderable that it cannot be weighed.

Before Berzelius knew potash-chloride of palladium, he tried to precipitate palladium by cyanide of mercury, but he found that by this process a solution of palladium containing copper yielded a greenish precipitate, assuming a dark hue after drying, and which contained copper. He could not find any other means of getting rid of this difficulty than by combining the metals with sulphuric acid, drying the solution, and gently igniting the residuum for a few moments, by which the salt of palladium was converted into a basic salt, insoluble in water. But this operation requires great care, because the heat, if too strong, decomposes the salt of copper, and if too feeble, leaves the salt of palladium undecomposed.

The roasted metallic sulphurets which the muriatic acid has not dissolved, are fused with bisulphate of potash until the flux ceases to acquire a colour. They contain much more rhodium than the potash-chloride of platinum precipitated at the beginning of the analysis, and they are treated in the manner described when we spoke of the latter, even respecting a small residuum of palladium, which is frequently met with in such a case. The mass which has been exhausted by repeated fusions with bisulphate of potash, is treated by aqua regia which dissolves a little platinum, and the oxyde of iridium is left behind.

The concentrated and boiled liquor, from which the metallic sulphurets have been precipitated, only contains iron in the state of protochloride of iron, a small quantity of iridium and of rhodium, and a trace of manganese. A sufficient quantity of nitric acid is poured into it, and the whole is boiled until the iron is completely peroxydised, of which the peroxyde of iron is precipitated by ammonia, washed, ignited, and weighed. This

peroxyde of iron contains iridium and rhodium, both in a state which admits of their dissolving with the peroxyde of iron in muriatic acid. In effecting this solution, a slight residuum of silicic acid is obtained, which is due to the decomposition of a silicious mineral contained in the ore of platinum, but the quantity of silica is generally too small to be taken into account. The peroxyde of iron is reduced by hydrogen gas, the metal is dissolved in muriatic acid, and heat is applied towards the end. There remains then a small quantity of an insoluble black powder. This powder contains the metals in a state which is not well known yet, because a very moderate heat is sufficient to cause them to decrepitate with a disengagement of light. Heated in close vessels, it gives much water, but does not produce any disengagement of light. After ignition in the open air it is weighed, and it has then the same degree of oxydise-ment as the peroxyde of iron. Its weight is to be deducted from that of the peroxyde of iron, and from the definitive weight of the latter that of the iron is calculated.

The liquor precipitated by ammonia contains still iridium and rhodium. After having added a quantity of carbonate of soda, sufficient to decompose the ammoniacal salts, it is evaporated to dryness, and the residuum is heated to incipient redness; the salt is then dissolved in water, which leaves the metallic oxydes in an insoluble state. If the residuum be heated too strongly, the saline liquor becomes yellow, and it then contains a small quantity of the oxydes. This mishap may, however, be avoided, by using only a moderate heat. The quantity of manganese which exists in the metallic oxydes, is scarcely more considerable than is strictly necessary to identify this metal, and if the experiment is performed upon two grammes, it is imponderable. It is extracted from the washed oxydes by treating them by muriatic acid.

In order to avoid a multiplicity of little operations, Berzelius makes a reserve of the oxydes of rhodium, and of iridium obtained from the peroxyde of iron, and from the saline mass, and adds them to the sulphurets which have to be treated

by the bisulphate of potash. They are then analysed together.

\* *Another method* of analysing the ores of platinum, has been indicated by Döbereiner: it is grounded upon this, that iridium, rhodium, copper, iron, and to a great extent palladium, are precipitated from their solutions, in the dark, by milk of lime, or by lime-water, whilst this effect takes place with platinum only when the liquor is exposed to solar light.

In order to dissolve the ore of platinum, Döbereiner proceeds in the ordinary way, with this difference only, that he at once uses the whole of the nitric acid which is apparently necessary for the treatment of the ore, and adds, subsequently, the suitable quantity of muriatic acid, but gradually. When the latter acid has undergone complete decomposition, that is, when all its chlorine has been taken up by the metal, the heated contents of the retort begin to spirt, and every time this takes place, it is a proof that more muriatic acid is wanted. The product of the distillation, after being rectified, is almost completely saturated with milk of lime, or with an alkali, and then treated, whilst boiling, by formiate of alkali, which produces a disengagement of carbonic acid, and the deposit of a blue powder, which is metallic osmium (page 227).

The solution of the ore of platinum is filtered, and the residuum in the retort is washed also on a filter. The matter remaining on the filter after washing and drying, is tested by ammonia, in order to see whether it contains any chloride of silver. Should it contain any, this chloride should be extracted by ammonia; the residuum should then be ignited with the filter, and weighed.

The filtered solution of the ore, together with the water used for washing, is mixed in a dark place, with a thin milk of lime, until the liquor is almost neutral. A large excess of lime-water is then added to it, and the whole is filtered as rapidly as possible in a dark place, washed with cold lime-water, and the precipitate is collected on a filter. The filtered liquor contains

all the chloride of platinum produced, a little protochloride of palladium, and so much dissolved lime, that, when exposed to solar light, it resolves into a liquid containing chloride of calcium, and of platinate of lime. It is slightly acidified with muriatic acid, (which removes the turbidness, if any was produced,) and it is put in contact with metallic zinc, in a warm place. After the complete separation of the platinum, which is recognised by the colourless state of the supernatant liquor, the zinc is freed from the platinum which adheres thereto, by means of a feather, and dilute muriatic acid; the precipitated platinum is likewise washed with muriatic acid, in order to free it from the zinc which might remain mixed with it, after which, and without throwing the platinum on a filter, which might occasion a small loss, it is washed in the vessel which contains it, with boiling water, and treated by nitric acid, which must be completely free from muriatic acid: the palladium is thereby dissolved. The platinum thus separated from the nitric acid liquor, and well washed, resembles almost completely, by its properties, that which is obtained by reducing a solution of platinum by means of organic substances. As it absorbs oxygen, like spongy platinum, though in a less degree, it should be ignited, which operation converts into carbonic acid the carbon which it contained, and which it derived from the zinc employed. The ignition must take place in a covered platinum crucible, because otherwise the deflagration which takes place might project a small portion of substance out of the vessel.<sup>1</sup>

The nitric acid liquor which contains palladium is almost neutralised with carbonate of soda, and precipitated by cyanide of mercury; the precipitate is washed and preserved moist upon the filter, until the time has come to add thereto the cyanide of palladium and that of copper, which will be obtained at a later period.

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<sup>1</sup> From the examination to which M. Claus, *Journ. für Pract. Chem.* xxxii., has submitted Döbereiner's method, it would appear that it cannot be employed where great accuracy is required, because the other metals, and especially peroxyde of iron, which may be present in the solution, are precipitated along with the oxyde of platinum.—Ed.

\* If the mixture of platinum and palladium reduced by the zinc has not been well washed after treatment by nitric acid, the presence of muriatic acid will cause a small portion of platinum to be dissolved, which, under the influence of a salt of zinc, is precipitated by cyanide of mercury when the liquor comes to be heated ; wherefore the operator should be on his guard.

\* The precipitate which hydrate of lime and lime-water produce in the solution of the ore of platinum, and which has been washed with lime-water, is dissolved whilst still moist in muriatic acid, after which the palladium and a small quantity of copper which it contains are precipitated by cyanide of mercury. If the solution is acid it must first be neutralised by carbonate of soda. The precipitate produced by cyanide of mercury is added to the cyanide of palladium previously obtained ; the whole is well washed, dried, and burnt with the filter. The ignited mass, which consists of palladium and copper, is dissolved in nitric acid, which ordinarily leaves a slight residuum of carbon. The acid solution is to be nearly saturated with carbonate of soda, and heated in a capacious vessel with a formiate of alkali and a little free acetic acid, by which the palladium is reduced in the midst of a very tumultuous disengagement of carbonic acid. When the disengagement of the gas has ceased, and a fresh addition of formiate of alkali fails in producing an effervescence, the salt of palladium is completely reduced. The palladium is then well washed, dried, and weighed. As to the copper contained in the liquor separated from the palladium by means of the formiate of alkali, it may be determined by precipitating it by means of hydrate of potash.

\* The filtered liquor, after precipitating it by cyanide of mercury, is added to the water used for washing the precipitate, and after pouring some muriate of ammonia into it, is evaporated to dryness. The residuum is treated by alcohol of sp. gr. 0·833, in which the ammonia-chlorides of iridium and of rhodium are insoluble, when the liquor contains still some perchloride of iron. During the evaporation of the aqueous solution, crystals of ammonia-chloride of rhodium mixed with a very

## CHAPTER XXXI.

GOLD.  

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## DETERMINATION OF GOLD AND OF OXYDE OF GOLD.

GOLD is determined quantitatively from its solutions by reducing it, which may be effected in various ways. This reduction may be effected by means of the solution of a salt of protoxyde of iron, or by that of protochloride of iron. The solution ordinarily employed for the purpose is that of protosulphate of iron, which precipitates gold from its solutions under the form of a fine brown powder. When the solution contains only perchloride of gold, muriatic acid should be added in order to keep in solution in the free acid the peroxyde of iron produced by the prolonged action of the atmospheric air upon the solution of the protosalt of iron, and thus prevent its being precipitated along with the reduced gold. The solution of the protosalt of iron reduces gold completely, yet it is good, after having poured it in that of the latter, to leave the whole at rest for some time in a moderately warm place. The gold is then collected on a filter, gently ignited and weighed. The ignition may take place in a platinum crucible.

When the solution of gold contains nitric acid still, which occurs ordinarily, because it is customary to dissolve gold and many of its alloys in aqua regia, the reduction of the metal must be carried on more carefully, for it might happen that the aqua regia contained in the solution would redissolve a small portion



of the reduced gold. In such a case it is advisable, before adding the protosulphate of iron to evaporate the liquor, until all the nitric acid will have evaporated and chlorine begins to disengage. Muriatic acid is gradually added to the liquor whilst it is undergoing concentration, by heating it for a long time; the nitric acid is thus destroyed and chlorine is disengaged. The solution is then diluted with water, and a sufficient quantity of protosulphate of iron is added. If the liquor has been evaporated to dryness, free muriatic acid, as well as water, should be added to the dry residuum. If some gold had almost separated from the liquor during the evaporation, and before the solution of protosulphate of iron was poured in, it does not matter, this always taking place when the evaporation is carried so far that chlorine begins to be disengaged, and subchloride of gold formed.<sup>1</sup>

Gold may also be reduced from its solution, by adding a solution of subnitrate of mercury; this method, however, is not so good as the preceding. It is necessary in such cases that the solution should not contain too much nitric acid, and the precipitate produced must be ignited in order to expel all the mercury.

In a great many cases the reduction of gold may be advantageously effected by means of *oxalic acid* and of the *oxalates*. When a solution of oxalic acid is employed, the gold is reduced slowly but completely. The solution of gold should be left to digest with the oxalic acid in a warm place for a long time, from 24 to 48 hours being requisite. So long as the reduction of the metal is taking place, there is a disengagement of carbonic acid,

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<sup>1</sup> When gold exists in a solution which contains other metals as well, protosulphate of iron does not precipitate the gold completely, as was observed by M. Elsner (*Annales de Chimie et de Physique*, January, 1844). Zinc, however, precipitates all the gold completely; but if copper, silver, tin, tellurium, antimony, cadmium, platinum, palladium, rhodium, iridium, or arsenic, be present, they may be precipitated at the same time; wherefore the processes described subsequently for the separation of the gold from the other metals which may have been precipitated with it, must be resorted to.—ED.

on which account the operator should watch the process, that nothing may be lost by projection. The gold reduced by this process is under the form of small yellow scales, which, when the metal is not abundant, adhere to the sides of the vessel, and is not precipitated in the form of powder, as when protosulphate of iron is employed to effect the reduction.

If the operator wishes to employ an oxalate for the purpose of reducing gold, he can employ only one of those the base of which forms with muriatic acid a metallic chloride soluble in water, and which, in presence of nitric acid, are capable of forming salts soluble in that acid. In all cases, however, the solution must contain enough free muriatic acid to be able to decompose the oxalate. If the liquor contains too much nitric acid, it may happen, as when protosulphate of iron is employed to effect the reduction, that a small portion of the reduced gold dissolves in the aqua regia; it should therefore be treated as we have said above, in order to expel the nitric acid.

Many other substances, especially those called *organic*, may precipitate gold in the metallic state, but those which we have mentioned seem to claim the preference. In presence of an excess of potash, almost all organic substances precipitate gold from its solutions in the metallic state, and under the form of a black powder.

When a solution contains nothing but gold, unmixed with any other metal, it might be evaporated to dryness, and the residuum being ignited, would consist of metallic gold only, if no other substance capable of resisting the action of the fire was present. But in such a case the gold being spread upon the whole surface of the vessel, cannot be detached without much trouble, and is much more difficult to gather than when it has been precipitated by a substance capable of reducing it.<sup>1</sup>

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<sup>1</sup> Chloride of antimony also reduces gold from a solution of chloride of gold; the precipitated gold has an exceedingly fine metallic colour.—Ed.

SEPARATION OF GOLD AND PEROXYDE OF GOLD FROM OTHER  
METALS AND METALLIC OXYDES.

\* Several methods may be adopted for separating gold from other metals. If gold be contained in the state of perchloride or peroxyde of gold in a solution, it may be separated from a great number of metals by acidifying the said solutions by means of muriatic acid and pouring therein a solution of protosulphate of iron or of oxalic acid. The oxydes of the metals which have a great affinity for oxygen are not precipitated by these reagents. In the majority of such cases, oxalic acid is preferable to protosulphate of iron for reducing gold, because, after having separated the reduced metal by filtering the liquor, it is more difficult to determine the oxydes of the other metals when that liquor contains in solution a large quantity of iron, which should first be eliminated.

When *oxalic acid* is the reagent chosen for effecting the separation of gold from other metals with which it is dissolved, the operator must not forget to add a sufficient quantity of muriatic acid. A very great number of metallic oxydes form with oxalic acid, combinations which are insoluble, or very sparingly soluble in water, but which dissolve in muriatic acid, provided this acid be in sufficient quantity.

After having filtered the reduced gold from the liquor, the substances which were combined with the gold or with the peroxyde of that metal, are determined in the manner described before. Gold may then be separated from copper, uranium, bismuth, cadmium, nickel, cobalt, zinc, iron, manganese, or from the oxydes of these metals, also from the earths and from the alkalies. This method cannot be resorted to when gold has to be separated from large quantities of silver or of lead, because the chlorides of these two metals are insoluble, or very sparingly soluble in acid liquors. Neither can oxalic acid be recommended for separating gold from platinum; though the latter is not capable of being precipitated in the metallic state by oxalic acid, as is the case with gold.

*Sulphuretted hydrogen* precipitates gold completely from a dilute acid solution, and this reagent is therefore useful for separating it from substances which cannot be precipitated from an acid solution by sulphuretted hydrogen, which, however, should not be passed through the liquor whilst hot, and the black sulphuret of gold produced must be rapidly filtered, because delay would convert the sulphur of the sulphuret into sulphuric acid, which would remain in the liquor whilst the gold would separate in the metallic state. The sulphuret of gold is dried, and roasted in a platinum crucible, the sulphur is thus volatilised, and gold remains, the weight of which may be determined. This method may serve to separate gold from nickel, cobalt, zinc, iron, manganese, the earths, and the alkalies, which might exist in solution with it.

\* Sulphuret of gold being soluble in an excess of hydrosulphuret of ammonia,<sup>1</sup> this reagent may be resorted to for separating gold in solution, not only from the substances which have been enumerated, but from several metals which are precipitated in the state of metallic sulphurets by hydrosulphuret of ammonia, from their acidified solutions, and which sulphurets are not soluble in hydrosulphuret of ammonia, such as, for example, copper, bismuth, cadmium, and lead. The *modus operandi* is as follows :—If the solution be dilute, it must first be concentrated; it is supersaturated with ammonia, and a pretty large excess of hydrosulphuret of ammonia is poured upon the precipitate which has been produced. The whole is left at rest in the vessel, which the operator must keep covered, until the sulphuret of gold which will have formed is completely redissolved. The undissolved metallic sulphurets are collected on a filter, and washed with water containing a little hydrosulphuret of ammonia. The gold is then precipitated from the solution by supersaturating it with dilute muriatic acid; it is dried, ignited,

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<sup>1</sup> The hydrosulphuret of ammonia, however, must then contain an excess of sulphur, for persulphuret of gold is insoluble in the colourless hydrosulphuret of ammonia.—Ed.

and the weight of the metallic gold left behind is determined. The metals of the metallic sulphurets dissolved by the hydro-sulphuret of ammonia are separated by means of the methods which have been described before.

Considering that gold is not soluble in the simple acids, pure nitric acid, diluted, and in some cases, pure muriatic acid, might be employed for separating it from other metals with which it might be alloyed, since most of them are soluble in nitric acid, and some of them are likewise soluble in muriatic acid. The operator should not, however, use too strong or boiling nitric acid, because the nitrous acid which is then produced might dissolve a very slight proportion of gold.

Yet the operator must not lose sight of this fact, that several metals, such as silver and lead, are easily dissolved by nitric acid, when alone, or alloyed with other metals, but the alloys of which with gold are difficultly attacked by that acid, especially when they contain a large proportion of this metal, and the operator has omitted to reduce them into thin leaves. It is better, therefore, when an auriferous alloy has to be quantitatively alloyed, and provided such an alloy does not contain much silver or lead, to dissolve it in aqua regia, to expel the nitric acid from the solution, either by means of muriatic acid, or by the action of heat, and then to precipitate the gold, to perform which operation, as we observed before, oxalic acid is the most suitable reagent.

#### SEPARATION OF GOLD FROM PLATINUM.

Gold and platinum cannot be separated from each other, except by concentrating their aqua regia solution, adding 60 per cent. of its bulk of alcohol, and then pouring a concentrated solution of muriate of ammonia, or, better still, of chloride of potassium into it. A precipitate of potash-chloride of platinum, or of ammonia-chloride of platinum, is formed, whilst a potash, or ammonia-chloride of platinum remains dissolved in the alcohol, without being reduced by it, provided the liquor does not

accidentally contain an excess of potash. The precipitate is washed with weak alcohol, to which a small quantity of a concentrated solution of muriate of ammonia or of chloride of potassium is added, after which the quantity of platinum which it contains is determined in the manner described before (page 239). The filtered liquor is then to be gently heated, in order to volatilise the greatest part of the alcohol, and the gold is precipitated therefrom by means of a solution of protosulphate of iron, or, better still, by oxalic acid.

\* Iridium may be separated from gold in the same manner.

\* This method is preferable to that which consists in fusing the alloy of gold and of platinum with three times its weight of silver, and treating the product by nitric acid. After fusion with silver, platinum dissolves in nitric acid, whilst the gold remains untouched.<sup>1</sup>

#### SEPARATION OF GOLD FROM SILVER.

The separation of these two metals is of very great importance in a technological point of view, and may be effected in various ways. It is generally executed by melting, with a known weight of pure silver, the alloy, the constituents of which have been approximately ascertained beforehand, by a trial with the touchstone. The quantity of silver contained in the alloy, united with that which has been added, must be about three times or three and a half times more considerable than that of the gold. The fusion is performed upon a cupel in a cupelling furnace, after having added to the mass three or four times its weight of pure lead,<sup>2</sup> because the heat of the furnace is not powerful enough to melt completely the gold and the silver.

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<sup>1</sup> According to M. Kemp, the separation of gold and of platinum may be effected very easily, by means of oxalic acid, as follows :—To the solution containing the gold and the platinum a solution of oxalic acid is added, which reduces the gold whilst the platinum remains in solution. The precipitated gold being removed, formic acid is added to the filtered liquid, which reduces the platinum and precipitates it completely.—Ed.

<sup>2</sup> The lead employed should be reduced from litharge or acetate of lead.—Ed.

The lead is then cupelled, taking care to raise the temperature as little as possible, in order that the protoxyde of lead produced should carry as little gold as possible in the cupel. The operation being finished, the alloy of gold and silver produced is beaten into a thin leaf, which is to be rolled up, heated to redness, and then moderately heated in a matras with pure nitric acid, diluted. The silver only is dissolved, whilst the gold remains. When the acid no longer dissolves anything, it is decanted; pure nitric acid of a greater strength is poured on the residuum, the whole is boiled, the liquor is decanted, the residuum is repeatedly washed with distilled water, and the washing is to be continued so long as a precipitate of chloride of silver is produced by testing with muriatic acid. The gold which remains retains the form which the alloy possessed before being submitted to the action of the nitric acid. It is to be moderately ignited, in order to give it more solidity, and it is then weighed. The loss indicates the quantity of silver.

\* It is necessary, in this experiment, to operate only on a very small quantity of the alloy, for example, half a gramme, for when the analysis is performed on larger proportions, the result is less accurate.

\* This method, known under the name of *quartation*, is employed only when the alloy under examination contains a considerable quantity of gold proportionably to that of silver. It is in effect the only case in which silver cannot be separated from gold by nitric acid alone, for when the proportion of the gold in the alloy is small, and does not form more than one-third or one-fourth of that of the silver, the alloy may be treated by pure nitric acid, without any further addition of silver, after having hammered or laminated it as we said above.

\* For scientific purposes, the analysis is performed in a different manner. If the alloy contains very little silver, for example, not more than about 15 per cent., it is best to laminate it, weigh it, and treat it by aqua regia, heating the whole for a long time. The gold dissolves completely, and the

silver is transformed into chloride of silver, a portion of which is dissolved, it is true, by the strong acid, but is completely precipitated by adding a sufficient quantity of water to the liquor; the chloride of silver produced retains the form of the alloy upon which the experiment was performed. It is carefully divided with a glass tube, the liquor is diluted with a large quantity of water, heat is applied, and when all the chloride of silver has settled at the bottom, it is collected on a filter and weighed. The filtered liquor is evaporated until the nitric acid which it contains has disappeared; the gold is precipitated by means of oxalic acid, and after having separated it by filtering, the oxydes in solution in the liquor, and the metals which might be combined with the gold or the silver in the alloy, are determined. These metals ordinarily consist in native alloys, of only small proportions of copper and of iron.

\* This method, however, cannot be advantageously adopted when the quantity of the silver in the alloy is more considerable, that is to say, when it is above 15 per cent. When such an alloy is treated by aqua regia, even after having hammered it into thin leaves, the chloride of silver produced envelopes the, as yet, unattacked portion so completely, that it altogether shelters it from the action of the acid. In such a case pure nitric acid must be employed instead of aqua regia, but the use of this acid is suitable only for the analysis of alloys containing much more silver than gold; that is to say, those in which the latter metal is not above about 20 per cent. The compound is to be flattened without rolling it, and weighed; nitric acid is poured upon it, and when the acid has exhausted its action, which should be promoted by applying heat, the remaining gold should be divided as much as possible by a glass tube in order to be certain that the whole of the silver has been dissolved, whilst in the assays which have been described for practical purposes, the operator endeavours to preserve the form of the rolled leaf, in order to economise the time in weighing. The divided gold is collected on a filter, well washed, dried, ignited, and weighed. It should also be dissolved in aqua regia, in order to



ascertain that the solution is perfectly free from silver, and does not yield any trace of chloride of silver, by diluting it with water.

\* To the solution which has been filtered from the gold, muriatic acid is added, in order to precipitate the silver in the state of chloride of silver. After having collected it on a filter, the oxydes existing in the liquor and the metals which existed in the alloy may be determined. If, however, by dissolving the gold in aqua regia, the operator has ascertained that it contains silver still, this solution may be mixed with the liquor filtered from the gold, which precipitates the silver in the state of chloride of silver. This precipitate is then collected on a filter, the gold contained in the filtered liquor is reduced; in fine, the process is the same as we have described before (after the treatment of the alloy by aqua regia).

\* When, however, an alloy contains more than 15 but less than 80 per cent. of silver, neither of the methods which have been previously described can be employed in scientific analysis. The method described (page 262) yields results which are satisfactory only when performed by practised hands, but which otherwise are so often uncertain that they are of no practical value even for commercial purposes.

\* When we wish to make a rigorously accurate analysis of an alloy of gold which contains between 15 and 80 per cent. of silver, the method which consists in fusing it with an exactly weighed quantity of pure silver, and treating the fused mass by pure nitric acid, is not applicable, on account of the difficulty of fusing the alloy with the silver in a small crucible in a furnace, for in operating in this manner the sides of the crucible very often absorb very small globules of the fused mass, which it is then extremely difficult to collect together, neither can the fused alloy be freed from all trace of the substance of the crucible by means of a file, because it is absolutely necessary that the whole of the fused metals be submitted to the analytical process, since the fusion is not uniform, and the composition varies in different

parts of the mass. On the other hand, the fusion is not successfully effected without lead, upon a small cupel in the muffle of a cupelling furnace, because the heat is not sufficient for the purpose.

\* It is therefore preferable to employ a metal more fusible than silver for dissolving the alloy, in order to be able to treat it by nitric acid alone. The most suitable metal to effect this is pure lead, which may be procured by igniting the acetate of lead of commerce. According to my brother's experiments, by fusing about three parts of this lead with one part of alloy of gold and silver in a small porcelain crucible upon an argand spirit-lamp, an alloy is obtained completely decomposable by pure nitric acid without it being necessary to laminate it. It is treated by this acid until nothing remains but pure gold, which, for greater security, should be redissolved in aqua regia, in order to make sure that the solution contains no silver. The liquor filtered from the gold is now treated so as to precipitate the oxyde of silver dissolved in the state of chloride of silver. When dilute muriatic acid is employed to effect this precipitation, it may happen, if the liquor is not very dilute, that chloride of lead will fall down with the chloride of silver. It is true that it may be eliminated by protracted washings, but the separation is difficult. It is therefore more convenient, instead of muriatic acid, to employ a solution of chloride of lead for the purpose of precipitating the chloride of silver from the liquor.

\* If a small quantity of chloride of silver has been formed whilst the gold was dissolving, it is collected on a filter, after having first diluted the liquor with water. The chloride of silver which is subsequently precipitated by chloride of lead from the liquor filtered from the gold may be collected on the same filter. Considering that the solution of the gold in aqua regia may contain a very small quantity of chloride of lead, it is advisable in such a case, after having eliminated the nitric acid, to precipitate the gold, not by oxalic acid, but by a solution of a protosalt of iron; and as a solution of protosulphate of iron cannot be employed, because the gold reduced might then be mixed with sulphate of lead, the best is to use a solution of protochloride of iron to effect this reduction.

\* By this method, it is difficult to determine the small quantities of iron, and of copper, or of other metals, which may be contained in a natural alloy of gold, or of silver. When we wish to ascertain the exact quantity of these metals, it is well to treat a portion of the alloy by another analytical process, which does not give, it is true, the exact quantity of silver, but which at any rate, permits the operator to determine, with sufficient precision, that of the other constituents. The alloy is hammered into a very thin leaf, of which a given weight is treated by aqua regia. When a crust of chloride of silver has formed upon the, as yet, unattacked portion of the alloy, and the action of the acid has ceased, even though the whole be strongly heated, the liquor is decanted, that which remains of the leaf is washed with water, and the crust of chloride of silver which adheres to its surface, is dissolved by ammonia. The ammoniacal solution is added to that previously obtained in aqua regia, which, if the latter be acid, precipitates chloride of silver from it. The remainder of the leaf of alloy is again treated by aqua regia, then by ammonia, and these two operations are repeated, until the whole of the alloy be dissolved. After having put all the liquors together, and diluted them with water, all the chloride of silver formed is collected on a filter, taking care, however, to ascertain, beforehand, that the solution is acid. The gold is then reduced from the filtered liquor, by means of oxalic acid, and after having filtered it from this metal, the small quantities of the other metallic oxides which may still exist in the solution are determined.

\* This method is very complicated, and therefore should not be resorted to except when an alloy of gold, or of silver, contains other metals besides. The quantity of muriate, and of nitrate of ammonia, which are formed by the mixture of the liquors, is not sufficient to precipitate the chloride of silver in a complete manner, therefore, it is prudent to take another portion of the alloy, and to analyse it in the manner which has been described before, that is, by fusing it with lead, and separating the metal mass by nitric acid.

## SEPARATION OF GOLD FROM COPPER.

For technical purposes, the quantity of gold contained in an alloy of gold and silver is determined by weighing the compound, fusing it upon a cupel in a cupelling furnace, with three or four times its weight of pure lead, and subsequently cupelling it. The remaining gold is weighed, and the copper is calculated from the loss sustained.

\* If the alloy under examination, besides gold and copper contains silver also, which compounds are of more importance in the arts than those which contain gold and copper only, the operator takes a given weight of the alloy, in which the quantity of the gold has been first approximatively determined by means of the touchstone; a sufficient quantity of pure silver, exactly weighed, equal to three or four times that of the gold, is added to it, and the whole is fused with three or four times its weight of pure lead upon a cupel, in a cupelling furnace, and the fused mass is submitted to cupellation. When the copper and the lead have been completely oxydised, and absorbed by the cupel, the remaining alloy of gold and silver is weighed; the loss indicates the quantity of the copper. In order, afterwards, to separate the gold from the silver, the method, by means of nitric acid, which has been previously described, is resorted to, and after deducting the silver which has been added, the operator calculates from the loss the quantity of that which was contained in the alloy.

\* As these methods do not yield very accurate results, they cannot be employed for scientific purposes, though, in a commercial point of view, they are sufficiently exact. From that which I have said, the operator may know how to separate gold both from copper alone, and from silver and copper.<sup>1</sup>

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<sup>1</sup> That is to say, gold can be separated from copper by means of oxalic acid, as was said, or else, this process requiring a long time, the acid solution of the gold may be neutralised with soda or potash, and sulphurous acid being added and the whole boiled, the gold is reduced and precipitates in the form of spangles, whilst the copper remains in solution.—Ed.

## CHAPTER XXXII.

## TIN.

## DETERMINATION OF TIN AND OF ITS OXYDES.

WHEN tin is combined in the metallic state with other metals, the method ordinarily employed to determine its quantity, consists in boiling it with nitric acid, in order to convert it into peroxyde of tin, which is insoluble in that acid. When, on the contrary, it exists in the state of protoxyde of tin in a solution, nitric acid is added thereto, and the liquor is concentrated by boiling; the protoxyde is thus converted into peroxyde of tin, which is insoluble, both in nitric, and in sulphuric acids. If, however, the liquor contains a large quantity of muriatic acid, a little peroxyde of tin is dissolved by it. In such a case, a sufficient quantity of nitric acid is added to the solution, and it is concentrated by evaporation, until the muriatic acid is partly destroyed, partly volatilised. The insoluble peroxyde of tin thus obtained is collected on a filter, ignited, and weighed.

The process is the same when the solution contains peroxyde of tin; it is likewise boiled with nitric acid, reduced to a small bulk by evaporation, and the peroxyde of tin produced is separated by filtering. Even when the liquor contains that sort of peroxyde of tin which is obtained from perchloride of tin, and which is partly soluble in cold nitric acid, by boiling it with nitric acid, the other modification of peroxyde of tin, which is insoluble in nitric acid, is obtained. Yet, this result requires that the mixture of nitric acid and of the solution of perchloride of tin

should have been brought to perfection by a somewhat further stage of concentration. The compound is in the main prepared of tin from which some other decomposition is made, and is not a mixture.

\* Peroxyde of tin may be prepared directly by adding a solution of stannous chloride to a solution of nitric acid, and adding a solution of potassium permanganate. The peroxyde may be collected on a filter and completely washed with cold water. It is ignited in the air and a tetroxy collected and reserved for use.

\* When a solution contains tin it is completely oxidized by peroxide of tin, and a solution of stannous chloride is formed by the action of nitric acid. To convert it to peroxide, and to collect the tin, add a solution of stannous chloride to the solution of peroxide of tin, and the solution of stannous chloride is completely oxidized to peroxide of tin, and the solution of stannous chloride is completely oxidized to peroxide of tin, and the solution of stannous chloride is completely oxidized to peroxide of tin.

\* Even sulphuric acid may be completely eliminated from peroxide of tin by washing. The tin is dissolved in nitric acid, and the solution is completely oxidized to peroxide of tin, and the solution of peroxide of tin is completely oxidized to peroxide of tin, and the solution of peroxide of tin is completely oxidized to peroxide of tin.

\* Whether tin exists in the state of peroxide or of peroxide in a solution, it may be completely separated therefrom by means of sulphuretted hydrogen, taking care first to dilute it with a sufficient quantity of water when it is neutral or when it contains a free acid. Sulphuretted hydrogen determines in solutions of protoxide of tin a brown precipitate, which is a proto-sulphuret of tin, and in solutions of persalts of tin, a yellow precipitate of persulphuret of tin. The latter settles much more slowly than the other. When peroxyde of tin has been precipitated from a solution by sulphuretted hydrogen, and the liquor is fully saturated with the gas, the portion of the gas in the free

bismuth, it is advisable to add some nitric acid to the water used for washing, in order to prevent the admixture of a basic salt of bismuth to the peroxyde of tin. Tin may be thus separated from its metallic combinations with silver, copper, bismuth, lead, cadmium, nickel, cobalt, zinc, iron, and manganese.

If the alloy contains platinum and gold, it might, perhaps, be treated by chlorine gas in an apparatus similar to that described (page 212); perchloride of tin would thus be produced, which would volatilise, and its vapours would be dissolved by the water contained in the flask. The gold and platinum would remain combined with more or less chlorine, according to the temperature at which the experiment may have been performed.

SEPARATION OF THE OXYDES OF TIN FROM THE OXYDES OF URANIUM, OF NICKEL, COBALT, ZINC, IRON, AND MANGANESE, FROM THE EARTHS AND THE ALKALIES.

All those substances which are not precipitated by sulphuretted hydrogen from acid solutions, may be separated from the oxydes of tin, not only by nitric acid, but likewise by sulphuretted hydrogen. Yet, it is advisable in most cases to use muriatic acid for acidifying the solutions. If the combinations of the oxydes in question with tin are in the solid form, the operator should try to disunite them by muriatic acid. If they be insoluble or very sparingly soluble in this acid, they may, in many cases, after careful pulverisation, be dissolved in concentrated sulphuric acid, diluted with a small quantity of water. The solution may then be moderately diluted with water, and the oxydes of tin are then precipitated by sulphuretted hydrogen. But if the combination is likewise insoluble in sulphuric acid, it must be ignited with three or four times its weight of carbonate of potash or of soda, after which the mass will dissolve in muriatic acid.

For analysing an alloy of tin and of copper (gun-metal bronze), Sobrero employs dry chlorine, a current of which is

\* When the quantity of the tin dissolved in the state of sulphuret in hydrosulphuret of ammonia, is not very considerable, and the liquor contains no other fixed substances besides, it may be evaporated to dryness, and the residuum cautiously ignited, by which means the sulphuret of tin is converted into peroxyde of tin.

If the solution contains peroxyde, or protoxyde of tin, and oxyde of silver, hydrosulphuret of ammonia, or nitric acid, should be used to separate their oxydes from each other, by the process which has been described before. The result is not accurate when muriatic acid is poured in the acid liquor, to precipitate the oxyde of silver in the state of chloride of silver, because it often happens that a little peroxyde of tin falls down with the chloride of silver.

DETERMINATION OF THE RELATIVE PROPORTIONS OF PROTOXYDE,  
AND OF PEROXYDE, OF TIN, WHEN THESE TWO OXYDES  
EXIST SIMULTANEOUSLY.

When a solution contains simultaneously protoxyde and peroxyde of tin, or protochloride and perchloride of tin, and the operator wishes to determine the quantities of both, the best method is the following:—The solution of tin is gradually poured in a solution of perchloride of mercury, a portion of which is converted by the oxyde of the protochloride of tin into subchloride of mercury, which separates under the form of a crystalline scaly precipitate. This precipitate is collected on a weighed filter, dried at a very gentle heat, and weighed. From this weight, it is easy, with the help of the tables, to calculate the quantity of protoxyde, or of protochloride of tin, existing in the liquor.

The quantity of tin contained in another portion of the liquor, is determined by treating it by one of the methods which have been indicated before, and preferably by sulphuretted hydrogen. It is then easy, from the quantity of the tin obtained, to calculate that of the perchloride, or of the peroxyde of tin.

In precipitating the subchloride of mercury, it is necessary to



pour the solution of tin drop by drop, in that of the perchloride of mercury, and not *vice versa*. It is also necessary that there should be an excess of perchloride of mercury, because, otherwise, the subchloride might, in either case, be reduced into metallic mercury. Lastly, it is necessary to heat the whole, and to suffer a long time to elapse before collecting the subchloride of mercury.

## CHAPTER XXXIII.

## TITANIUM.

## DETERMINATION OF TITANIC ACID.

AMMONIA is the best reagent for precipitating titanium from the solutions in which it exists in the state of titanic acid. The precipitate is bulky, and resembles that of alumina. A large excess of ammonia should be avoided, which might leave extremely small traces of titanic acid in solution ; wherefore it is advisable, after having precipitated by ammonia, to leave the whole at rest in a warm place, until the greatest part of the excess of the volatile alkali has evaporated. The voluminous precipitate of titanic acid shrinks very much in drying. When dry it is ignited, which operation is accompanied by a disengagement of light, and weighed. Ignition imparts a great lustre to it, and a slightly brownish hue. The weighing must take place in a well closed platinum crucible, as soon as it has cooled, because otherwise, the titanic acid absorbing moisture, would increase a little in weight.

Titanic acid has very often been precipitated from its acid solutions by boiling the liquor for a long time, by which means the titanic acid became insoluble in the acid in which it was in solution, and was thus obtained in the form of a heavy precipitate. But though the liquor may be boiled ever so long, it always retains a certain quantity of titanic acid, which can be obtained only by evaporating the whole to dryness. In filtering

the titanic acid precipitated by ebullition, the liquor passes clear through the filter so long as it is acid, but the moment one attempts to wash it with pure water, the filtrate becomes milky, and ultimately carries all the titanic acid, so that at last none of it remains on the filter, even though it may be made of strong paper. This difficulty can be obviated only by using acidulated water for the washing, but this always dissolves a little titanic acid. The only case in which, according to Berzelius, titanic acid can be wholly precipitated by boiling when the liquor has been diluted with a great quantity of water, is when it exists in solution in sulphuric acid.

The reasons just mentioned oppose the separation of titanic acid from other substances by boiling the acid solution in which these other substances remain dissolved. Even though the titanic acid may have been totally precipitated, which is not the case, this method of analysis could not be adopted. Some chemists have proposed to wash the titanic acid precipitated by ebullition with solution of ammoniacal salts, asserting that this prevented the liquor from passing milky through the filter; but this does not prevent it, or else the titanic acid blocks up the pores of the filtering paper, so that the washing cannot be carried on. By adding a little ammonia to the water so used for washing, its passage through the filter may be facilitated, but when the substance which has to be separated from titanic acid is capable of being precipitated by ammonia, this addition evidently annihilates the object which this washing was intended for.

It has also been proposed, after having precipitated the titanic acid by ebullition, to evaporate the acid solution to dryness, or nearly so, and to treat the residuum with pure water or with acidified water; but all these methods are too imperfect to give results even approximatively accurate.

Wherefore, when titanic acid has to be quantitatively separated from foreign substances another method must be adopted; but this separation is often attended with so many difficulties,

that it is yet far from being effected in a rigorous and accurate manner.

\* When titanic acid has been ignited, it is as completely insoluble in muriatic acid as that found in nature under the name of rutile; if it is not then perfectly pure and the quantity of foreign substances mixed with it has to be determined, it should be levigated, mixed in a platinum crucible with three or four times its weight of carbonate of potash or of soda, and the whole is ignited. The calcining must be effected slowly and with moderation, for if the heat were too strong and applied too rapidly, the titanic acid would expel the carbonic acid from the alkaline carbonate too rapidly, and a loss might be sustained by projection. In fusing titanic with the alkaline carbonates the same precaution must be taken as during the fusion of silicic acid or of the silicates with these substances. We shall describe fully these precautions farther on. The titanate of alkali which is thus obtained is completely soluble in dilute muriatic acid; heat must be eschewed during this solution.

\* The titanic acid and the substances which were combined with it is determined in the liquor.

In order to render calcined titanic acid soluble in acids, it may also be heated with concentrated sulphuric acid diluted with its own bulk of water, and when the titanic has dissolved, the solution is diluted with water. This process may be employed to dissolve rutile, and in general all the combinations of titanic acid which are insoluble in acids.

#### SEPARATION OF TITANIC ACID FROM THE OXYDES OF TIN, OF GOLD, OF PLATINUM, OF OSMIUM, OF IRIDIUM, PALLADIUM, MERCURY, SILVER, COPPER, BISMUTH, LEAD, AND CADMIUM.

As titanic acid is not precipitated from acid solutions by sulphuretted hydrogen, it may be separated from all the above oxydes by means of this reagent, which precipitates them from their acid solutions in the state of metallic sulphurets.

SEPARATION OF TITANIC ACID FROM THE OXYDES OF COBALT,  
OF ZINC, OF IRON, AND OF MANGANESE.

The following method may be employed to separate titanic acid from the oxydes, which, like those of cobalt, zinc, iron, manganese, are precipitated from a neutral or alkaline solution by hydrosulphuret of ammonia in the state of metallic sulphuret. To the solution, which ordinarily is acid, a solution of tartaric acid is added, which prevents not only titanic acid, but nearly all the oxydes by which it may be accompanied, from being precipitated by ammonia. The solution is then supersaturated by ammonia, which produces no precipitate provided enough tartaric acid has been employed. To this ammoniacal liquor hydrosulphuret of ammonia is added, which precipitates the other oxydes in the state of metallic sulphurets whilst the titanic acid remains in the solution. The metallic sulphurets are collected on a filter, and washed with water, to which a little hydrosulphuret of ammonia has been added. The quantity of the oxydes contained in the solution may be determined from these sulphurets in the manner which has been described before.

It is now more difficult to determine the quantity of the titanic acid contained in the filtered liquor. If this liquor contains no other fixed substance besides titanic acid, the excess of hydrosulphuret of ammonia needs not be destroyed by the addition of an acid; it is immediately evaporated to dryness, and the residuum is ignited in contact with the air in a platinum crucible, or capsula of a known weight, until all the volatile substances have evaporated, and the carbon of the tartaric acid is completely burnt. There remains titanic acid only, the weight of which may be determined. It is difficult, however, to burn the carbon completely in a platinum crucible by an argand spirit-lamp; but this combustion is easily and completely effected by putting the counterpoised platinum crucible in the muffle of a small assay furnace. If the tartaric acid employed contained dry lime, which is always the case with that obtained

## CHAPTER XXXII.

TIN.  

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## DETERMINATION OF TIN AND OF ITS OXYDES.

WHEN tin is combined in the metallic state with other metals, the method ordinarily employed to determine its quantity, consists in boiling it with nitric acid, in order to convert it into peroxyde of tin, which is insoluble in that acid. When, on the contrary, it exists in the state of protoxyde of tin in a solution, nitric acid is added thereto, and the liquor is concentrated by boiling; the protoxyde is thus converted into peroxyde of tin, which is insoluble, both in nitric, and in sulphuric acids. If, however, the liquor contains a large quantity of muriatic acid, a little peroxyde of tin is dissolved by it. In such a case, a sufficient quantity of nitric acid is added to the solution, and it is concentrated by evaporation, until the muriatic acid is partly destroyed, partly volatilised. The insoluble peroxyde of tin thus obtained is collected on a filter, ignited, and weighed.

The process is the same when the solution contains peroxyde of tin; it is likewise boiled with nitric acid, reduced to a small bulk by evaporation, and the peroxyde of tin produced is separated by filtering. Even when the liquor contains that sort of peroxyde of tin which is obtained from perchloride of tin, and which is partly soluble in cold nitric acid, by boiling it with nitric acid, the other modification of peroxyde of tin, which is insoluble in nitric acid, is obtained. Yet, this result requires that the mixture of nitric acid and of the solution of perchloride of tin

should have been brought by evaporation to a somewhat high state of concentration. The separation of the insoluble peroxyde of tin then takes place under disengagement of ruddy fumes of nitrous acid.

\* Peroxyde of tin may also be precipitated tolerably well from a solution, by saturating the latter with ammonia, and adding a solution of *succinate of ammonia*. The precipitate may be collected on a filter, and completely washed with cold water. It is ignited in the air, and is thereby converted into peroxyde of tin.

\* When a solution contains no other constituents than protoxyde or peroxyde of tin, it is advisable, after having treated it by an excess of nitric acid, to evaporate it to dryness, and to calcine the dry mass in a platinum crucible. After ignition, pure peroxyde of tin remains, because the action of the fire has dissipated the acids when they are of a volatile nature in the free state.

\* Even sulphuric acid may be completely eliminated from peroxyde of tin by calcining. Yet it is advisable, after having ignited the peroxyde of tin in a platinum crucible and weighed it, to place upon it a small piece of dry carbonate of ammonia and to ignite it again strongly, and to weigh the oxyde a second time. By adopting this precaution the last traces of sulphuric acid or of any other volatile acid are driven off.

\* Whether tin exists in the state of protoxyde or of peroxyde in a solution, it may be completely separated therefrom by means of *sulphuretted hydrogen*, taking care first to dilute it with a sufficient quantity of water when it is neutral, or when it contains a free acid. Sulphuretted hydrogen determines in solutions of protosalts of tin a brown precipitate, which is a protosulphuret of tin, and in solutions of persalts of tin, a yellow precipitate of persulphuret of tin. The latter settles much more slowly than the other. When peroxyde of tin has been precipitated from a solution by sulphuretted hydrogen, and the liquor is fully saturated with the gas, the portion of the gas in the free

state retains in solution a small quantity of sulphuret of tin, which, however, is totally precipitated when the liquor is left to digest at a gentle heat until it does not exhale the slightest smell of sulphuretted hydrogen. If the solution contained protoxyde of tin only, the sulphuret of tin produced when the liquor is saturated by the gas, settles much more rapidly, and should be collected on a filter whilst the liquor exhales the odour of the gas.

\* The sulphuret of tin obtained in this manner might be collected on a filter, and, after having dried it, the quantity of peroxyde or the protoxyde of tin might be determined from its weight. When, however, the operator does not know the degree of oxydisation of the tin in the solution, or when the liquor contained a mixture of both oxydes, this method is inapplicable.

\* The best and the simplest method of determining how much tin the sulphuret of tin contains, consists in converting it into peroxyde of tin, from the weight of which that of the metal may be calculated. The *modus operandi* is as follows:—After drying the precipitate, which needs not be completely done, the sulphuret of tin is put in an open platinum crucible and gently heated therein, until the odour of sulphurous acid can no longer be perceived. When this moment has arrived, the heat is then increased to redness. If the yellow sulphuret were at once strongly heated, it would lose half its sulphur and be converted into black sulphuret, which fuses easily, powerfully attacks the platinum crucible, and is, after fusion, difficultly converted into peroxyde of tin, whilst this conversion is completely effected when the roasting is carried on very slowly, and at too low a temperature to fuse the sulphuret.

There is no harm in not converting the whole of the black sulphuret into peroxyde of tin, for these two substances have nearly the same atomic weight. The only real inconvenience is the damage to the platinum crucible.

A small piece of carbonate of ammonia is placed upon the peroxyde obtained, which must have a white colour, and the



crucible is strongly heated. If this produces a small loss of weight the operation must be repeated, until after igniting and weighing it twice successively the weight remains the same. The carbonate of ammonia expels from the peroxyde of tin the last traces of the sulphuric acid produced by the roasting.

Peroxyde of tin is found in nature, mixed with a very small proportion of foreign substances, but in such a state of density that it is insoluble in acids. This is the case with the artificial peroxyde of tin after ignition. When the operator wishes to determine quantitatively the small proportion of foreign substances mixed with the native peroxyde of tin, the compound must be levigated and mixed with three times its weight of carbonate of potash or of soda, and the whole must be ignited. Carbonic acid is disengaged from the alkaline carbonate, owing to which the mixture should be gradually heated. The same precautions must be observed as for the fusion of silicic acid, or of the silicates with the alkaline carbonates, and which I shall fully describe farther on. After fusion with the alkali the peroxyde of tin has become soluble in acids. The quantity of peroxyde of tin in the solution may then be determined, as well as that of the foreign substances by which it was accompanied.

#### SEPARATION OF TIN FROM OTHER METALS.

The separation of tin from other metals is not very difficult. If it be an alloy it is boiled with nitric acid. All the metals which have been hitherto enumerated, with the exception of those called noble, such as platinum, gold, &c., are oxydised by nitric acid, and the oxydes dissolve in this acid, except peroxyde of tin. The best is to evaporate the nitric acid solution with the undissolved peroxyde of tin, until the excess of nitric acid is mostly volatilised; water is added, the peroxyde of tin is collected on a filter, and its quantity is determined as we have said. The oxydes dissolved in the liquor are determined by the methods which have been indicated for each of them in the preceding pages. If the alloy contained

bismuth, it is advisable to add some nitric acid to the water used for washing, in order to prevent the admixture of a basic salt of bismuth to the peroxyde of tin. Tin may be thus separated from its metallic combinations with silver, copper, bismuth, lead, cadmium, nickel, cobalt, zinc, iron, and manganese.

If the alloy contains platinum and gold, it might, perhaps, be treated by chlorine gas in an apparatus similar to that described (page 212); perchloride of tin would thus be produced, which would volatilise, and its vapours would be dissolved by the water contained in the flask. The gold and platinum would remain combined with more or less chlorine, according to the temperature at which the experiment may have been performed.

SEPARATION OF THE OXYDES OF TIN FROM THE OXYDES OF URANIUM, OF NICKEL, COBALT, ZINC, IRON, AND MANGANESE, FROM THE EARTHS AND THE ALKALIES.

All those substances which are not precipitated by sulphuretted hydrogen from acid solutions, may be separated from the oxydes of tin, not only by nitric acid, but likewise by sulphuretted hydrogen. Yet, it is advisable in most cases to use muriatic acid for acidifying the solutions. If the combinations of the oxydes in question with tin are in the solid form, the operator should try to disunite them by muriatic acid. If they be insoluble or very sparingly soluble in this acid, they may, in many cases, after careful pulverisation, be dissolved in concentrated sulphuric acid, diluted with a small quantity of water. The solution may then be moderately diluted with water, and the oxydes of tin are then precipitated by sulphuretted hydrogen. But if the combination is likewise insoluble in sulphuric acid, it must be ignited with three or four times its weight of carbonate of potash or of soda, after which the mass will dissolve in muriatic acid.

For analysing an alloy of tin and of copper (gun-metal bronze), Sobrero employs dry chlorine, a current of which is

passed upon a given weight of the combination ; perchloride of tin is produced, which is volatile, and protochloride of copper remains.

SEPARATION OF THE OXYDES OF TIN FROM THE OXYDES OF  
MERCURY, OF SILVER, OF COPPER, OF BISMUTH, OF LEAD,  
AND OF CADMIUM.

These oxydes being capable of being precipitated from their acid solutions by sulphuretted hydrogen, may be separated from the oxydes of tin, by first supersaturating the solution with ammonia, and then pouring an excess of hydrosulphuret of ammonia into it, which dissolves the sulphuret of tin only, whilst the other metallic sulphurets are left.

Persulphuret of tin is much more soluble in hydrosulphuret of ammonia, than protosulphuret of tin. Could hydrosulphuret of ammonia be obtained perfectly free from all excess of sulphur, the latter might, perhaps, be insoluble in it. The best is to introduce the whole in a matras imperfectly closed with a cork, and to leave it to digest at a very gentle heat. The metallic sulphurets, which are insoluble in hydrosulphuret of ammonia separate, and the solution of the sulphuret of tin is more easily effected. If the tin existed in the solution in the state of protoxyde of tin, pulverised sulphur is added to the hydrosulphuret of ammonia, which converts it into persulphuret of tin, which is very soluble in this reagent. The metallic sulphurets which have refused to dissolve, are separated by filtering ; they are washed with water, containing a little hydrosulphuret of ammonia, after which, they are examined by the methods which have been indicated before, for the purpose of determining the quantity of the metals which they contain. To the filtered liquor, diluted with water, enough muriatic acid is added to render it slightly acid ; sulphuret of tin separates under a disengagement of sulphuretted hydrogen. The liquor is left to digest at a gentle heat, until it no longer exhales the odour of the gas, and the sulphuret of tin is separated by filtering, which is to be converted into peroxyde of tin, in the manner described above.

\* When the quantity of the tin dissolved in the state of sulphuret in hydrosulphuret of ammonia, is not very considerable, and the liquor contains no other fixed substances besides, it may be evaporated to dryness, and the residuum cautiously ignited, by which means the sulphuret of tin is converted into peroxyde of tin.

If the solution contains peroxyde, or protoxyde of tin, and oxyde of silver, hydrosulphuret of ammonia, or nitric acid, should be used to separate their oxydes from each other, by the process which has been described before. The result is not accurate when muriatic acid is poured in the acid liquor, to precipitate the oxyde of silver in the state of chloride of silver, because it often happens that a little peroxyde of tin falls down with the chloride of silver.

**DETERMINATION OF THE RELATIVE PROPORTIONS OF PROTOXYDE, AND OF PEROXYDE, OF TIN, WHEN THESE TWO OXYDES EXIST SIMULTANEOUSLY.**

When a solution contains simultaneously protoxyde and peroxyde of tin, or protochloride and perchloride of tin, and the operator wishes to determine the quantities of both, the best method is the following:—The solution of tin is gradually poured in a solution of perchloride of mercury, a portion of which is converted by the oxyde of the protochloride of tin into subchloride of mercury, which separates under the form of a crystalline scaly precipitate. This precipitate is collected on a weighed filter, dried at a very gentle heat, and weighed. From this weight, it is easy, with the help of the tables, to calculate the quantity of protoxyde, or of protochloride of tin, existing in the liquor.

The quantity of tin contained in another portion of the liquor, is determined by treating it by one of the methods which have been indicated before, and preferably by sulphuretted hydrogen. It is then easy, from the quantity of the tin obtained, to calculate that of the perchloride, or of the peroxyde of tin.

In precipitating the subchloride of mercury, it is necessary to

pour the solution of tin drop by drop, in that of the perchloride of mercury, and not *vice versa*. It is also necessary that there should be an excess of perchloride of mercury, because, otherwise, the subchloride might, in either case, be reduced into metallic mercury. Lastly, it is necessary to heat the whole, and to suffer a long time to elapse before collecting the subchloride of mercury.

## CHAPTER XXXIII.

## TITANIUM.

## DETERMINATION OF TITANIC ACID.

AMMONIA is the best reagent for precipitating titanium from the solutions in which it exists in the state of titanic acid. The precipitate is bulky, and resembles that of alumina. A large excess of ammonia should be avoided, which might leave extremely small traces of titanic acid in solution; wherefore it is advisable, after having precipitated by ammonia, to leave the whole at rest in a warm place, until the greatest part of the excess of the volatile alkali has evaporated. The voluminous precipitate of titanic acid shrinks very much in drying. When dry it is ignited, which operation is accompanied by a disengagement of light, and weighed. Ignition imparts a great lustre to it, and a slightly brownish hue. The weighing must take place in a well closed platinum crucible, as soon as it has cooled, because otherwise, the titanic acid absorbing moisture, would increase a little in weight.

Titanic acid has very often been precipitated from its acid solutions by boiling the liquor for a long time, by which means the titanic acid became insoluble in the acid in which it was in solution, and was thus obtained in the form of a heavy precipitate. But though the liquor may be boiled ever so long, it always retains a certain quantity of titanic acid, which can be obtained only by evaporating the whole to dryness. In filtering

the titanic acid precipitated by ebullition, the liquor passes clear through the filter so long as it is acid, but the moment one attempts to wash it with pure water, the filtrate becomes milky, and ultimately carries all the titanic acid, so that at last none of it remains on the filter, even though it may be made of strong paper. This difficulty can be obviated only by using acidulated water for the washing, but this always dissolves a little titanic acid. The only case in which, according to Berzelius, titanic acid can be wholly precipitated by boiling when the liquor has been diluted with a great quantity of water, is when it exists in solution in sulphuric acid.

The reasons just mentioned oppose the separation of titanic acid from other substances by boiling the acid solution in which these other substances remain dissolved. Even though the titanic acid may have been totally precipitated, which is not the case, this method of analysis could not be adopted. Some chemists have proposed to wash the titanic acid precipitated by ebullition with solution of ammoniacal salts, asserting that this prevented the liquor from passing milky through the filter; but this does not prevent it, or else the titanic acid blocks up the pores of the filtering paper, so that the washing cannot be carried on. By adding a little ammonia to the water so used for washing, its passage through the filter may be facilitated, but when the substance which has to be separated from titanic acid is capable of being precipitated by ammonia, this addition evidently annihilates the object which this washing was intended for.

It has also been proposed, after having precipitated the titanic acid by ebullition, to evaporate the acid solution to dryness, or nearly so, and to treat the residuum with pure water or with acidified water; but all these methods are too imperfect to give results even approximatively accurate.

Wherefore, when titanic acid has to be quantitatively separated from foreign substances another method must be adopted; but this separation is often attended with so many difficulties,

that it is yet far from being effected in a rigorous and accurate manner.

\* When titanic acid has been ignited, it is as completely insoluble in muriatic acid as that found in nature under the name of rutile; if it is not then perfectly pure and the quantity of foreign substances mixed with it has to be determined, it should be levigated, mixed in a platinum crucible with three or four times its weight of carbonate of potash or of soda, and the whole is ignited. The calcining must be effected slowly and with moderation, for if the heat were too strong and applied too rapidly, the titanic acid would expel the carbonic acid from the alkaline carbonate too rapidly, and a loss might be sustained by projection. In fusing titanic with the alkaline carbonates the same precaution must be taken as during the fusion of silicic acid or of the silicates with these substances. We shall describe fully these precautions farther on. The titanate of alkali which is thus obtained is completely soluble in dilute muriatic acid; heat must be eschewed during this solution.

\* The titanic acid and the substances which were combined with it is determined in the liquor.

In order to render calcined titanic acid soluble in acids, it may also be heated with concentrated sulphuric acid diluted with its own bulk of water, and when the titanic has dissolved, the solution is diluted with water. This process may be employed to dissolve rutile, and in general all the combinations of titanic acid which are insoluble in acids.

SEPARATION OF TITANIC ACID FROM THE OXYDES OF TIN, OF GOLD, OF PLATINUM, OF OSMIUM, OF IRIDIUM, PALLADIUM, MERCURY, SILVER, COPPER, BISMUTH, LEAD, AND CADMIUM.

As titanic acid is not precipitated from acid solutions by sulphuretted hydrogen, it may be separated from all the above oxydes by means of this reagent, which precipitates them from their acid solutions in the state of metallic sulphurets.



SEPARATION OF TITANIC ACID FROM THE OXYDES OF COBALT,  
OF ZINC, OF IRON, AND OF MANGANESE.

The following method may be employed to separate titanic acid from the oxydes, which, like those of cobalt, zinc, iron, manganese, are precipitated from a neutral or alkaline solution by hydrosulphuret of ammonia in the state of metallic sulphuret. To the solution, which ordinarily is acid, a solution of tartaric acid is added, which prevents not only titanic acid, but nearly all the oxydes by which it may be accompanied, from being precipitated by ammonia. The solution is then supersaturated by ammonia, which produces no precipitate provided enough tartaric acid has been employed. To this ammoniacal liquor hydrosulphuret of ammonia is added, which precipitates the other oxydes in the state of metallic sulphurets whilst the titanic acid remains in the solution. The metallic sulphurets are collected on a filter, and washed with water, to which a little hydrosulphuret of ammonia has been added. The quantity of the oxydes contained in the solution may be determined from these sulphurets in the manner which has been described before.

It is now more difficult to determine the quantity of the titanic acid contained in the filtered liquor. If this liquor contains no other fixed substance besides titanic acid, the excess of hydrosulphuret of ammonia needs not be destroyed by the addition of an acid; it is immediately evaporated to dryness, and the residuum is ignited in contact with the air in a platinum crucible, or capsula of a known weight, until all the volatile substances have evaporated, and the carbon of the tartaric acid is completely burnt. There remains titanic acid only, the weight of which may be determined. It is difficult, however, to burn the carbon completely in a platinum crucible by an argand spirit-lamp; but this combustion is easily and completely effected by putting the counterpoised platinum crucible in the muffle of a small assay furnace. If the tartaric acid employed contained dry lime, which is always the case with that obtained

from chemical works, the whole of this lime remains with the titanic acid, the weight of which is, of course, apparently very much reduced thereby. In such a case, the titanic acid obtained should be mixed with three or four times its weight of dry carbonate of potash or of soda, and the whole fused in a platinum crucible. Dilute muriatic acid is then poured upon the fused mass, which dissolves completely in it, provided heat has been avoided. The solution is diluted with water, and the titanic acid is precipitated therefrom by ammonia.

This method is principally applicable to separate titanic acid from the oxydes of iron, with which it is met with in native compounds. But as titanic acid is ordinarily united both with proto and peroxyde of iron simultaneously, the analysis must be executed upon two distinct portions of the compound. After having levigated and dried these two portions, the weight of which must be previously ascertained, they are put in a flask hermetically closed with a glass stopper, and they are dissolved therein by strong muriatic acid; the residuum left is very small, and consists of impure titanic acid. A solution of soda-chloride of gold is added in order to calculate from the quantity of the gold which precipitates that of the protoxyde of iron contained in the substance, according to the method which has been described (page 111). The precipitated gold is weighed and dissolved in weak aqua regia, which leaves impure titanic acid; this residuum is ignited, its weight is determined, and deducted from that of the mass, as if it were an unessential part of the combination. To the other solution, one of sulphuretted hydrogen is added in order to determine the quantity of peroxyde of iron, as we said (page 107). The sulphur obtained is weighed upon a counterpoised filter, and burnt. A small quantity of impure titanic acid is left, the weight of which is determined and deducted both from that of the sulphur and from that of the compound experimented upon. The liquor separated from the sulphur by filtering is mixed with tartaric acid, supersaturated with ammonia, and then hydro-sulphuret of ammonia is poured in, by which the iron is

precipitated in the state of sulphuret, which is afterwards converted into peroxyde of iron according to the process described (page 84), and from which the quantity of the iron in the substance is determined. The quantity of iron thus found must agree with that which is indicated by calculations in proto and in peroxyde of iron. The titanous acid may be afterwards determined in the liquor filtered from the sulphuret of iron.

\* Mosander follows *another method* of analysis for the combination of titanous acid with the oxides of iron. After having levigated the combination and dried the powder thus obtained, he weighs a portion of the latter, introduces it in a porcelain tube and ignites it therein in the midst of a stream of pure hydrogen gas, previously exsiccated by chloride of calcium, until water ceases to be produced by the decomposition of the oxides of iron, which period may be easily ascertained by means of a glass tube connected with that of porcelain, and in which the aqueous vapours carried off by the hydrogen gas are condensed. The tube is maintained at a red heat for half an hour after the moment when it is observed that water ceases being produced. The experiment is completed in about two hours and a half or three hours. The combination being withdrawn from the porcelain tube, must be put in a porcelain capsule, for if one of platinum were employed a small portion of the reduced iron would combine with the platinum. The loss of weight sustained by the combination indicates the quantity of the oxygen disengaged therefrom.

The residuum which is left to cool in the stream of hydrogen is found slightly agglomerated. It is weighed, treated by dilute muriatic acid, by which the iron is dissolved under disengagement of hydrogen gas. Yet it was necessary to employ stronger muriatic acid, and to leave the whole to digest in a warm place, in order to extract the last portions of the iron, because the presence of titanous acid prevented the reagent from coming in close contact with the metal. The titanous acid remains insoluble.

The iron in the muriatic acid solution is determined in the usual manner. If, besides the oxydes of iron and titanic acid, the combination contains other substances, they may be disengaged from the oxydes of iron by the methods which have been described before. After having evaporated to dryness the solution from which the peroxyde of iron has been precipitated, and ignited the dry mass, a small quantity of residuum, insoluble in muriatic acid, is sometimes obtained, which consists of titanic acid mixed with a little silicic acid.

The titanic acid undissolved by muriatic acid is never perfectly pure, and has a more or less lead-grey colour. Ignited in the open air, after having been first dried, it assumes a more or less deep rusty colour, and loses about one-half per cent. of its weight. The grey colour is therefore owing to the presence of a small quantity of carbon.

The titanic acid is afterwards dissolved by ebullition in concentrated sulphuric acid diluted with a little water. This acid sometimes leaves a small quantity of silicic acid.

The acid solution is evaporated in order to expel the excess of sulphuric acid. The residuum is dissolved in water, and the solution is treated by sulphuretted hydrogen, which precipitates a small quantity of sulphuret of tin. Tartaric acid is then added to the liquor, and supersaturated with ammonia; hydrosulphuret of ammonia precipitates therefrom slight traces of sulphuret of iron and sometimes of sulphuret of manganese.

According to Berthier, titanic acid may be separated from the oxydes of iron, and also from those of manganese, of zinc, of cobalt, of nickel, and of uranium, by the method which is employed for separating zirconia from the oxydes of iron (page 93).

#### SEPARATION OF TITANIC ACID FROM ZIRCONIA.

The greatest difficulties are met with when the object in view is the separation of titanic acid from substances which cannot be precipitated in the state of metallic sulphurets by sulphuretted

hydrogen, or by hydrosulphuret of ammonia, but which are precipitated like titanous acid by ammonia. Titanous acid is often met with in nature, combined with some of these substances, especially with zirconia. We are as yet in possession of no method by which the two oxides may be quantitatively separated from each other, on account of the many properties which are common to both of them.

SEPARATION OF TITANOUS ACID FROM THE OXIDES OF CERIUM  
AND FROM YTTRIA.

Titanous acid is likewise difficult to separate from the oxides of cerium and from yttria, which two substances it is often met with in a combined state in nature. The only way of separating it from these substances is by boiling the solution for a long time in sulphuric acid diluted with water, by which means the titanous acid is precipitated. After having collected the latter upon a filter, the oxides of cerium and the yttria are separated from the filtered liquor in the manner which has been described (page 65). The separation cannot be effected by means of carbonate of ammonia, because titanous acid is not absolutely insoluble in that reagent.

SEPARATION OF TITANOUS ACID FROM GLUCINA AND ALUMINA.

Titanous acid may be separated from glucina and alumina in the same manner. The separation cannot be effected by solution of pure potash, because titanous acid is not entirely insoluble therein.

SEPARATION OF TITANOUS ACID FROM MAGNESIA.

Titanous acid may be separated from magnesia by means of ammonia, after having added muriate of ammonia to the liquor in sufficient quantity to prevent the precipitation of the magnesia.

**SEPARATION OF TITANIC ACID FROM LIME.**

Titanic acid may very well be precipitated from lime by means of ammonia. Titanic acid is found combined with lime in the mineral called sphene or titanite. It is only necessary, pending the filtering, to shelter the precipitated titanic acid from the contact of the air, in order to prevent its being contaminated by carbonate of lime.

**SEPARATION OF TITANIC ACID FROM STRONTIA AND FROM BARYTA.**

Titanic acid may be separated from these earths by sulphuric acid, by which the latter substances are both precipitated.

**SEPARATION OF TITANIC ACID FROM THE ALKALIES.**

Ammonia is the reagent employed to separate titanic acid from the fixed alkalies.

\* When titanic acid is combined with the fixed bases, these combinations are soluble in muriatic acid, even after ignition. This takes place, for example, with the combinations of titanic acid with protoxyde of iron, peroxyde of iron and lime which are found in the native state. The combinations of titanic acid with potash and soda which are manufactured, are soluble likewise in muriatic acid, even after ignition, provided they do not contain too little alkali and too large a proportion of titanic acid. In order to render the native titanates soluble in this acid they should be reduced to fine powder by levigation, and dried at a gentle heat; they are then weighed, and strong muriatic acid is poured upon them in a flask capable of being hermetically closed with a glass stopper. They are, it is true, dissolved thereby very slowly, but yet completely. Ordinarily there remains a small quantity of impure titanic acid, the quantity of which is determined. By applying a very moderate heat, these titanates dissolve more rapidly in muriatic acid, but great caution is then required, because a stronger heat would precipitate the dissolved titanic acid in an insoluble state.

The combinations which are not very soluble in muriatic acid are rendered more easily soluble therein, by reducing them into very fine powder and fusing them with carbonate of potash or of soda, and treating the fused mass by muriatic acid, or by digesting them in concentrated sulphuric acid, as we said before.

## CHAPTER XXXIV.

## ANTIMONY.

## DETERMINATION OF ANTIMONY AND OF ITS OXYDES.

WHETHER antimony exists in solutions in the state of oxyde of antimony, antimonious, or antimoniac acid, it cannot be precipitated therefrom in a complete manner except by passing a current of sulphuretted hydrogen through the diluted acid liquor, by which an orange-red precipitate of sulphuret of antimony is produced. When the solution contains oxyde of antimony, the precipitate has a brick-red colour; if it contains antimonious or antimoniac acid, the colour of the precipitate inclines to yellow, but these tinges depend upon the greater or less state of dilution of the liquor, so that in certain circumstances a precipitate of sulphuret of antimony obtained from a solution of antimoniac acid may be altogether red, which happens especially when the solution of the antimoniac acid has been effected by organic acids only, and not by muriatic acid, in which case, that is, if muriatic acid is altogether absent, the antimony is difficultly precipitated in a complete manner from the solution, by sulphuretted hydrogen, and not less difficultly washed with pure water.

As the concentrated acid solutions of antimony are generally decomposed and yield a white precipitate by dilution with water, it is advisable before pouring water to add pure tartaric acid thereto in sufficient quantity. After this addition they may be diluted to any degree without their becoming milky. It is prudent to adopt this precaution as much as possible, for it is



always better to pass sulphuretted hydrogen through a clear solution than through a milky liquor, because in the latter case it may often happen that a portion of the precipitate, especially when it is heavy, escapes the action of the sulphuretted hydrogen.

After having passed sulphuretted hydrogen to perfect supersaturation, so that it smells strongly of the gas, it is left at rest in a moderately warm place until the odour of sulphuretted hydrogen has disappeared. This precaution is indispensable, because the liquid saturated with sulphuretted hydrogen retains in solution pretty considerable traces of sulphuret of antimony, which are entirely precipitated when the whole of the sulphuretted hydrogen has escaped. This is especially the case when the solution contained antimonious or antimonic acid, but less so when it is oxyde of antimony. The sulphuret of antimony is collected upon an exactly counterpoised filter, washed with pure water, and dried at an extremely gentle heat until it ceases to lose weight, and it is then weighed.

It is only in a very small number of cases that the quantity of antimony can be calculated from the weight of the sulphuret of antimony. It can be done only when the operator knows in a positive manner that the metal existed in the solution in the state of oxyde of antimony. Now this is the case only when oxyde of antimony, or the sulphurets of that metal, have been dissolved in concentrated muriatic acid; but even then the sulphuret of antimony contains a certain quantity of sulphur in excess which has separated from the solution, and which comes from the free sulphuretted hydrogen dissolved therein, and which the air decomposes, so that in such a case the determination of antimony as sulphuret is uncertain. In aqua regia solutions the product is always a mixture of several degrees of oxydisation of antimony, and in presence of tartaric acid the precipitate obtained from the solutions of antimonious acid is a sulphuret of antimony which does not correspond to this degree of oxydisation of the metal, but one which corresponds to that of antimonic acid.

When, however, the quantity of antimony or of oxyde of

antimony has to be determined from the weight of a dry sulphuret of antimony precipitated from a solution of antimonic acid, the operator must never neglect to treat a small quantity of it by concentrated muriatic acid ; if it dissolves completely in this acid with disengagement of sulphuretted hydrogen, we may be certain that it corresponds to peroxyde of antimony, but if a residuum of sulphur is obtained, the operator must examine how much antimony a known weight of sulphuret contains, and determine from it the total quantity of the metal. This research must always be made when the antimony existed at a higher degree of oxydisation in the liquor from which it has been precipitated by sulphuretted hydrogen gas.

There are two methods of determining how much antimony the sulphuret obtained contains, between which the operator may choose. One of these methods is the following : After having weighed accurately the dry sulphuret with the filter, as much of it as can be removed from the filter without rubbing it, is put in a matras ; the filter is then weighed with that which may still adhere to it, in order to ascertain with precision the quantity of sulphuret upon which the experiment will be performed.

Fuming nitric acid is poured in the matras drop by drop, and with the utmost care, so as to avoid the projection which might result from too violent an action of the acid. A larger proportion of nitric acid is then poured in, and as much muriatic acid as is sufficient to dissolve the antimony in a complete manner is added. If instead of fuming nitric acid a weaker nitric acid or moderately strong aqua regia was used, it might happen that a slight trace of sulphuretted hydrogen would be disengaged from very fine particles of the sulphuret of antimony in a great state of division, which should be carefully guarded against. A weaker nitric acid, however, may be employed to oxydise the sulphuret of antimony, only the operator must in that case heat it almost to ebullition before pouring it on the sulphuret ; muriatic acid is subsequently added, in order to dissolve in a complete manner the antimony which has thus been oxydised.

The aqua regia is then left to digest on the sulphuret until the sulphur remains of a pure yellow colour, or until it is altogether dissolved. Ordinarily the sulphur is oxydised in a complete manner when strong fuming nitric acid has been employed, or if any of it remains, the quantity is always very slight; a suitable quantity of muriatic acid is then added to the liquor; it is then diluted with water, and the sulphur which may have remained undissolved is collected upon a very small filter, dried with care at an extremely gentle heat, and its weight is determined. A solution of chloride of barium is poured in the filtered liquor until it ceases to produce a precipitate; the whole is then very moderately heated, in order that the precipitated sulphate of baryta may settle well. It is collected on a filter and washed. In this case the washing of the sulphate of baryta produced requires a long time, on account of the presence of nitric acid; warm water should be used for the purpose. When the salt is dry it is ignited and the weight is determined, from which the operator calculates the quantity of sulphur which it contains. When some sulphur has remained in an insoluble state during the treatment of the sulphuret by aqua regia, its quantity is added to that which exists in the sulphate of baryta. The whole of the sulphur is then deducted from the quantity of sulphuret upon which the experiment has been performed, and the operator thus learns how much antimony this sulphuret contained.

\* If the quantity of tartaric acid, added to the solution of oxyde of antimony, is very considerable, the precipitated sulphate of baryta contains a little tartrate of baryta, which cannot be eliminated, even by the most careful washing. This tartrate is converted into carbonate of baryta by ignition. Wherefore, in rigorously accurate analysis, it is necessary, if the quantity of the sulphate of baryta is at all considerable, to digest it in dilute muriatic acid, after previously igniting and weighing it. The solution is filtered, and by adding a few drops of sulphuric acid, the baryta in solution is precipitated in the state of sulphate, the weight of which is ascertained and from

which, that of the carbonate may then be known and deducted from that of the sulphate of baryta, obtained in the first instance.

The *other method* of determining the quantity of antimony contained in the sulphuret, consists in weighing a certain quantity of sulphuret, and heating it in an atmosphere of hydrogen, by which means, metallic antimony is obtained, the weight of which is determined. In order to effect this, an apparatus similar to that for the reduction of oxyde of cobalt, represented, page 128, is employed. After having dried the sulphuret of antimony upon a weighed filter, and weighed the sulphuret itself, the greatest portion of it is introduced into an accurately weighed apparatus, consisting of a glass-bulb, on each side of which a glass tube is soldered. The whole portion is introduced into the bulb, and the tubes on each side of the glass bulb are cleaned with the feather of a pen. The apparatus is then weighed, in order to ascertain the weight of the sulphuret about to be treated. Everything being ready, a current of dry hydrogen gas is passed through the apparatus, and when filled with it, the bulb containing the sulphuret of antimony is gradually heated. If the composition of the latter is such that it corresponds to that of oxyde of antimony, the whole of the sulphur is converted into sulphuretted hydrogen, and the antimony remains; if, on the contrary, it is a higher degree of sulphuration, or a mixture of several degrees of sulphuration, there remains metallic antimony likewise; but sulphur is first sublimed, and sulphuretted hydrogen is formed afterwards. The sulphur is deposited first at the upper part of the bulb, but on continuing the heat, and by the effect of the current of hydrogen, it is driven towards the extremity of the glass tube at the end of the apparatus. By means of a small spirit-lamp, this sulphur is expelled from the tube as fast as it sublimes, and when the operator perceives that no more sulphur is volatilised, and that the production of the sulphuretted hydrogen has ceased, the apparatus is suffered to cool, the current of hydrogen

being continued during the time. When the apparatus has completely cooled, it is taken to pieces, and the loss of weight was sulphur, the remainder is antimony.

\* When it is wished to convert sulphuret of antimony into metallic antimony, by means of hydrogen gas, the heat is removed, when, upon lighting the gas, the odour of sulphurous acid ceases to be smelt, or better still, when, by holding a glass rod, moistened with ammonia, at a short distance from the flame, no white clouds are produced.

This method gives an accurate result only, when the experiment is performed with the requisite care. It is impossible to prevent the sublimation of a small portion of antimony, which deposits at the upper part of the bulb, and which penetrates even in the tube, when the heat employed in the operation has been strong. If, on the contrary, the heat is too feeble, the sulphur is not totally expelled from the sulphuret of antimony. Moreover, the hydrogen really carries away an extremely slight quantity of antimony, owing to which, it burns towards the end with an almost imperceptible fume of antimony, and which deposits very slight traces of oxyde of antimony at the orifice of the tube at which the gas is inflamed. In consequence of this, it generally occurs that in most analyses the operator obtains a little less antimony, and a little more sulphur than should be obtained, because the quantity of the sulphur is calculated from the loss of weight. The quantity of antimony thus lost does not generally amount, however, to more than one quarter of a hundredth part at most, when the experiment has been conducted with proper care; with less care, it may amount to one half, or even to one per cent. The more slowly the sulphuret of antimony is heated at the beginning, the less is the quantity of the antimony volatilised. It is only towards the end that a stronger heat must be employed for a short time. The reduced antimony does not fuse into a lump, but remains in the form of small metallic grains. If, whilst the current of hydrogen gas is passing, the sulphuret has been gently heated for a long time, the antimony reduced presents crystalline facets, the lustre of

which makes the antimony appear of a blacker colour than that reduced under the influence of a stronger heat.

The high degrees of sulphuration of antimony might be reduced to the lower degrees, by heating them out of the contact of the air, and the quantity of the antimony might be calculated therefrom; but this process does not yield accurate results, both because the lowest degree of sulphuration of antimony is not perfectly fixed in the fire, and because the atmospheric air contained in the small retort, or matrass, which must be employed in the experiment, would form a little oxyde of antimony, which, uniting with the sublimed sulphur in the neck of the retort, would form a combination of sulphuret, and of oxyde of antimony. This difficulty, however, might be got over by heating the substance in an atmosphere of carbonic acid.

#### SEPARATION OF ANTIMONY FROM OTHER METALS.

As to the manner of separating antimony from other metals, a method often employed for the analysis of alloys, is that by nitric acid, which oxydises antimony, and leaves the oxyde of that metal in an insoluble state, whilst the oxydes of the other metals are dissolved by that acid. Yet, for the analysis of the alloys of antimony, nitric acid does not yield so accurate a result as that which is obtained when nitric acid is employed to separate tin from other metals. Oxyde of antimony is not as insoluble in nitric acid as peroxyde of tin, owing to which, the filtrate contains, besides the dissolved oxydes, pretty considerable traces of oxyde of antimony. The analysis of the combinations of antimony by nitric acid, gives a sufficiently exact result for technological, but it should not be employed for scientific purposes. The best method of isolating antimony from other metals, consists in dissolving the compound in aqua regia, and separating the dissolved antimony from the other metals by sulphuretted hydrogen, and hydrosulphuret of ammonia.

## SEPARATION OF ANTIMONY FROM TIN.

Antimony may be separated from the metals hitherto treated of, or its oxyde from their oxydes, by the methods which will be explained farther on, but which cannot be applied to tin, or its oxydes, because tin and antimony, as well as oxyde of antimony, and peroxyde of tin, are dissolved and precipitated by the same reagents.

According to Gay Lussac, the separation, and quantitative determination of these two substances may be effected as follows:—If the two metals are contained in a muriatic acid solution, and the operator knows their collective weight, an excess of muriatic acid is first added to the liquor, if it does not already contain one, and a blade of pure tin is immersed into it, which precipitates the antimony in the form of a black powder. The precipitation is not complete in the cold, or at any rate, a long lapse of time would be required; but by heating the liquor very gently upon a sand-bath, it is complete, provided an excess of acid be carefully maintained in the liquor. The antimony is then collected on a weighed filter, washed, and dried at a very gentle heat, and when quite dry, it is weighed. The loss indicates the quantity of the tin.

When the alloy to be analysed is one of antimony and tin, the alloy is first weighed, and dissolved in muriatic acid, to which small quantities of nitric acid are gradually added. If the two metals are contained in a solution, and their collective weight is not known, a known portion of the solution is taken, from which the two metals are simultaneously precipitated by means of a bar of zinc. The quantity of the antimony may be determined in another portion by means of a bar of tin.<sup>1</sup>

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<sup>1</sup> M. Levol, *Annal. de Chimie, et de physique*, xiii., has simplified the process of separation of tin and of antimony by muriatic acid, as follows:—The mixture of the metals is boiled for a few minutes in muriatic acid, and pending the boiling, a saturated and boiling solution of chlorate of potash is added, until the metal has dissolved; a bar of pure distilled zinc is then plunged into the solution, by which means both the tin and the antimony are precipitated in an extremely divided

SEPARATION OF ANTIMONY FROM MERCURY, SILVER, COPPER,  
BISMUTH, LEAD, CADMIUM, COBALT, ZINC, IRON, MANGA-  
NESE, GOLD, AND PLATINUM.

The oxydes which can be precipitated from acid solutions by sulphuretted hydrogen, may, for the most part, be separated from antimony, by treatment with hydrosulphuret of ammonia,

metallic state. The bar of zinc is freed from the metallic precipitate, and, without decanting the liquor from the precipitate, a fresh quantity of muriatic acid is added, which easily dissolves the tin, whilst the antimony remains in suspension, and can be collected. The tin is afterwards precipitated by means of sulphuretted hydrogen. This method cannot be used, however, where great accuracy is required, for Mr. Elsner has shown that some antimony is dissolved along with the tin by the muriatic acid.

Since the publication of the last edition of his work, H. Rose has indicated another method, which is quoted in the *Chemical Gazette*, as follows :—

“As it is well known, the separation of these two metals is accompanied with many difficulties. The older method of Claudet recommends the use of hydrochloric acid for this purpose ; but this is attended with success only when the action of the acid upon the antimony is weakened by the presence of a very large quantity of protochloride of tin. By this method, as also by that subsequently proposed by Gay Lussac, of precipitating the antimony from the solution of the two metals by means of metallic tin, the antimony alone is determined directly, and the amount of tin ascertained from the loss. Levol has, on this account, modified the process suggested by Claudet ; he dissolves the alloy of the two metals in hydrochloric acid, to which chlorate of potash has been added, precipitates both the metals from the solution by metallic zinc, and, without decanting the solution of chloride of zinc, redissolves, by the addition of highly-concentrated hydrochloric acid, the tin, which is then precipitated by sulphuretted hydrogen ; while antimony is left behind undissolved.

“This method has not been found to be accurate by Elsner, as some antimony is dissolved with the tin by the acid ; to which Levol has replied, that the presence of the chloride of zinc considerably weakens the action of the hydrochloric acid upon the antimony.

“Whichever method is employed, the separation of these two metals is never so perfect as with other substances which do not behave in so analogous a manner towards reagents as tin and antimony. The method which I employ, but which, to give satisfactory results, must be carried out with great care, is as follows :—

“Strong nitric acid is cautiously poured upon the metals, and, when the violent oxydation has ceased, the whole is evaporated at a gentle heat, and the dry powder of the oxydes fused in a silver crucible over an Argand lamp with an excess of hydrate of soda. The fused mass is softened with a large quantity of water, gently warmed, and the antimoniate of soda allowed to subside. When perfectly cold, the clear solution is passed through a filter ; if this is done while it is still warm, the solution will contain some antimoniate of soda. The insoluble salt is again treated



since all the degrees of sulphuration of antimony are soluble in this reagent. This method may likewise be employed to separate from the oxydes of antimony, those which are precipitated by hydrosulphuret of ammonia only from neutral or from alkaline solutions in the state of metallic sulphurets. It is done as follows:—The oxydised or metallic compound is put in

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once or twice with water, allowed to settle and cool, and the liquid, when perfectly clear, passed through the filter. When the whole of the stannate of soda has been dissolved in this manner, the liquid which has been warmed with the antimoniate of soda remains opalescent; it must not be poured upon the filter, as it would pass through turbid. A small quantity of a dilute solution of carbonate of soda may be added to it, which renders it clear; but theedulcoration must not be continued for any length of time, as otherwise some antimoniate would be dissolved.

“The moist antimoniate of soda is now treated in a beaker with a mixture of hydrochloric and tartaric acids, in which it readily dissolves; and the filter, upon which but mere traces of the salt should have collected, washed with the same mixture. The antimony is then precipitated from the solution by sulphuretted hydrogen, and the amount of antimony estimated from the quantity of sulphuret obtained. I am at present accustomed to reduce the sulphuret of antimony by hydrogen in a porcelain crucible, through the lid of which a thin porcelain tube passes. This apparatus is now manufactured at the royal porcelain works of Berlin. A gentle heat is carefully applied until the crucible no longer decreases in weight. After the reduction, the inner side of the lead is coated with metallic antimony, which might lead to the belief that the result of the experiments must be inaccurate, which, however, is not the case.

“The solution of the stannate of soda is acidified with hydrochloric acid. It is not requisite to add so much acid that the whole of the eliminated oxyde of tin is again redissolved. It is merely necessary that the solution should strongly redden blue litmus paper. Upon this, sulphuretted hydrogen is passed into it. The sulphuret of tin is converted, by roasting, into oxyde. When it has been dried it frequently decrepitates, which, by want of care, may occasion a very considerable loss. It is on this account preferable to place it with the filter, whilst still moist, in a porcelain crucible, and to heat it for a long time very gently and with access of air, to expel the sulphur at the lowest possible temperature. If a strong heat be given at the commencement, white fumes of oxyde escape, especially when the air has free access. The higher sulphuret of tin has the property of subliming somewhat at certain temperatures; the vapours are oxydised by contact with the air, and form oxyde of tin. This is also the cause of a white sediment of oxyde of tin being formed upon charcoal when sulphuret of tin is heated on charcoal before the blowpipe. A strong heat should not be applied until there is no longer any perceptible odour of sulphurous acid. After being strongly ignited, a piece of carbonate of ammonia is placed in the crucible; and, after its volatilisation, a strong heat applied with access of air, in order to expel the whole of the sulphuric acid formed. A small decrease in weight will be perceived.

“The oxyde of tin thus obtained never appears perfectly white; and the sulphuret of tin precipitated by sulphuretted hydrogen does not possess a purely yellow colour, which appears to arise from melting the metallic oxydes with hydrate of

a small matrass, and dissolved in concentrated muriatic acid ; if it is not totally soluble therein, which is almost always the case, aqua regia is employed instead. The concentrated solution is supersaturated in the matrass with ammonia, which ordinarily produces a very abundant precipitate, because nearly all the substances in the solution are thereby precipitated. A sufficient quantity of hydrosulphuret of ammonia is then added, and the matrass is corked up. Generally, a voluminous brownish-black precipitate is thus formed in the cold, because at first a great portion of the sulphuret of antimony produced separates with the other insoluble metallic sulphurets ; but by digesting the whole at a gentle heat, the precipitate gradually diminishes, and assumes a black colour.

The more free sulphur the hydrosulphuret of ammonia employed contains, the better is this separation effected, because the sulphuret of antimony is then more easily dissolved. It is therefore advisable to dissolve, beforehand, a small quantity of pulverised sulphur in the hydrosulphuret of ammonia. When the solution contains no manganese, zinc, or cadmium, and after the precipitate has become quite black, the whole may be suffered to cool completely, and it is filtered ; but it is necessary first to dilute it with water. The filtering and washing must be carried on without interruption, and the washing must be performed, not with pure water, but with water mixed with a little hydrosulphuret of ammonia. The filtered liquor holds the whole of the antimony in solution, in the state of sulphuret,

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soda in the silver crucible, traces of oxyde of silver being removed by the alkaline solution.

"The results do not attain the highest degree of accuracy. Although stannate of soda containing an excess of hydrate of soda does not become turbid by boiling, as stated by Frémy, and the solution may even be evaporated until crystals separate which entirely dissolve upon the addition of water, yet the antimoniate of soda contains a small quantity of oxyde of tin. Consequently, the sulphuret precipitated by sulphuretted hydrogen from the acid solution of the antimoniate of soda contains a small amount of sulphuret of tin, which does not part with the whole of its sulphur at the temperature at which the sulphuret of antimony is reduced by hydrogen. For this reason a somewhat smaller amount of tin, a larger quantity of antimony, and a slight excess, is found in the analysis."

from which it is precipitated by dilute muriatic acid, or by acetic acid, taking care to keep it slightly acid.

The sulphuret of antimony thus obtained is found mixed with the sulphur resulting from the decomposition of the excess of hydrosulphuret of ammonia. The liquor is left at rest upon the precipitate at an extremely gentle heat, until it no longer exhales the odour of sulphuretted hydrogen; the sulphuret of antimony is then collected upon a weighed filter and dried. When dry it is weighed and analysed by one of the two methods which have been described before. As to the metallic sulphurets which have been precipitated by hydrosulphuret of ammonia, they are dissolved and separated from each other by the methods which have been described before.

I must observe here, that before treating the compound to be analysed by hydrosulphuret of ammonia, it is absolutely necessary to dissolve it in acids, and to saturate the solution with ammonia. This precaution is, as we just said, absolutely necessary, even with oxydised compounds. And even when the substance has been reduced into fine powder, the hydrosulphuret of ammonia should not be immediately poured upon it, because the oxydes which are quite dry are not completely converted by this reagent into metallic sulphurets.

The metals which can thus be separated from antimony are manganese, iron, zinc, cobalt, cadmium, lead, bismuth, copper, silver, and mercury. When mercury is combined with antimony, the whole should, after having added hydrosulphuret of ammonia, be allowed to cool completely, and to settle for a long time before filtering. That which we have said here respecting the metals in general, applies to their oxydes.<sup>1</sup>

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<sup>1</sup> According to M. Brunner, *Poggendorf Annalen*, bd. xliv., the oxydes of antimony can be easily separated by combining them with sulphur. This is effected by fusing the compound with sulphuret of potassium or of sodium, and treating the fused mass by water, which takes up the sulphuret of antimony combined with the alkaline sulphuret, whilst the lead is left behind. The lead and the antimony may then be quantitatively determined in the usual manner.

Another method, proposed also by M. Brunner, consists in heating the compound of the two oxydes in a stream of sulphuretted hydrogen, by which means the two

\* Gold and platinum cannot be thus separated from antimony because their sulphurets are, like that of antimony, soluble in hydrosulphuret of ammonia.

*Another method* of separating antimony from most other metals is the following: After having weighed a certain quantity of the alloy, a current of chlorine gas is passed upon it by means of an apparatus similar to that represented page 212. If the alloy can be pulverised, it is better to employ it in the state of powder; if not, it should be reduced into pieces as small as possible. The glass bulb *e*, on each side of which the glass tubes are soldered, is weighed first empty, and then with the alloy to be examined. One of the two tubes is then to be bent at right angle, the apparatus is adjusted, and the bent tube is introduced into the flask *k*, which is half or two-thirds filled with a weak solution of tartaric acid, to which a little muriatic acid is added. The glass tube plunges only a little below the surface of the liquid. When the apparatus is full of chlorine gas, the glass bulb is to be heated with great care; the metals are thereby converted into metallic chlorides; the chloride of antimony, which is volatile, distils over, and is decomposed by the water in the flask. When the tartaric and muriatic acids are in sufficient quantity the liquor does not become milky. When no more volatile matter is disengaged the bulb is suffered to cool.

\* In these researches the analysis is exposed to become very inexact from the following circumstance, namely:—in the cold, most alloys of antimony are not sensibly attacked, but as soon as the compound begins to become hot it absorbs at once so much chlorine gas that it becomes red hot, and the liquor in the receiver may very easily ascend in the bulb *e*. It is therefore necessary, before beginning to apply heat to the alloy, to withdraw the tube, so that its orifice may be a little above the

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metals are obtained in the state of sulphurets, which are then to be heated in a current of muriatic acid gas; the chloride of antimony is thereby eliminated, whilst the chloride of lead is left. In the first of these methods, a porcelain crucible must be employed, the silica of which, however, contaminates the result.—ED.

surface of the liquid. As soon as a beginning of ignition is manifested in one part of the alloy, the lamp must be immediately removed.

When the experiment is ended, the greatest part of the glass tube bent at right angle is cut off and washed thoroughly with water, which is poured in the flask *k*. The liquor contained in this flask is diluted with water, and the antimony contained in it is precipitated in the state of sulphuret by means of sulphuretted hydrogen. The metallic chlorides in the glass bulb are weighed in order to determine their quantity. The operator may, however, dispense with this weighing when the alloy contains copper or some other metals the quantity of which cannot be calculated from the weight of the metallic chlorides obtained. The weighing is performed either by determining the weight of the apparatus after having cut part of the bent tube, then dissolving the chloride in water, and again weighing the empty apparatus; or by washing and thoroughly drying the cut off portion of the bent tube and weighing it with the glass bulb, by which means the weight of the metallic chlorides is determined, since the bulb had been weighed before. This latter process should be resorted to when the chlorides obtained are insoluble in water and in acids, as is the case, for example, with chloride of silver. The analysis of the metallic chlorides is performed according to the rules which have been indicated before. If the glass bulb contains any chloride of silver mixed with other metallic chlorides, the mixture is treated by water and a little acid, preferably by muriatic acid; a large quantity of water is then added, the whole is heated and the undissolved chloride of silver is separated by filtering, and its quantity is determined. The other metals are subsequently separated from the filtered liquors by the methods which have been described before, and their weight is determined.

This method may be employed to separate antimony from cobalt, nickel, lead, copper, silver, platinum, and gold; but when it contains lead, the operator must take care not to heat the bulb too strongly.

This method, however, is not so good as that which consists in precipitating antimony from its solutions by means of sulphuretted hydrogen, or in dissolving it by means of an excess of hydrosulphuret of ammonia. But this method, as we shall see farther on, is especially useful, or preferable to all others, for the purpose of separating sulphuret of antimony from other metallic sulphurets. The metallic alloys are more difficultly decomposed by chlorine than the sulphurets, and it often happens with many of them, when analysed by this reagent, that the remaining metallic chloride, if of a fusible nature, envelopes small portions of the undecomposed alloy, which it thus shelters from the action of the gaseous chlorine; this is the case more especially when the metallic compound cannot be pulverised.

Some chemists have tried to separate antimony from several of the metals called noble, especially *silver*, by cupelling it in the muffle of an assay furnace; by this treatment the antimony is converted into oxyde of antimony, and is dissipated in the form of smoke, whilst the silver remains behind, and is weighed. When, however, an alloy, solely composed of silver and antimony, is ignited in a bone cupel and kept in the muffle until no more fumes of antimony are perceived, the surface of the regulus of silver obtained, according to Bonsdoff, is greyish, and contains still about one per cent. of antimony, owing to which it is not completely soluble in nitric acid. But in cupelling this regulus a second time with about five times its weight of pure lead, until the brightening has appeared, the silver may be obtained quite pure.

\* Antimony might be separated from gold in the same manner.

SEPARATION OF ANTIMONY FROM OXYDE OF URANIUM, OF NICKEL,  
OF COBALT, OF ZINC, OF IRON, AND OF MANGANESE.

A better method than hydrosulphuret of ammonia for separating antimony in solution from the oxydes of uranium, of nickel, of cobalt, of zinc, of iron, and of manganese, consists in pouring tartaric acid in the acid liquor, diluting it with water,

and passing a current of sulphuretted hydrogen through it, in order to precipitate the antimony in the state of sulphuret, observing the rules and precautions which have been enumerated before. Yet the presence of tartaric acid in the liquor filtered from the sulphuret of antimony prevents the precipitation of the other oxydes by means of the reagents ordinarily employed for the purpose, for in most cases tartaric acid, when it exists in sufficient quantity, prevents potash from precipitating these oxydes. Wherefore the solution should be supersaturated with ammonia, and hydrosulphuret of ammonia being added thereto, will precipitate the oxydes in the state of metallic sulphurets. These sulphurets are to be dissolved and the quantity of the oxydes contained in the solution is determined by the methods which have been indicated before.

Oxyde of nickel is the most difficult of the oxydes to be thus determined, because hydrosulphuret of ammonia cannot precipitate it well in the state of sulphuret of nickel.<sup>1</sup> Wherefore, the precautions which have been indicated page 146, in treating of the precipitation of oxyde of nickel in the state of sulphuret of nickel must be observed, or else tartaric acid should not be used; and this acid should likewise be omitted when the oxydes of antimony have to be separated from the earths and the alkalies.

\* The method which consists in separating antimony from the oxydes mentioned at the beginning of the paragraph, by precipitating the acid solution by sulphuretted hydrogen, is preferable to that which consists in dissolving the sulphuret of antimony in hydrosulphuret of ammonia.

**\* SEPARATION OF THE OXYDES OF ANTIMONY FROM THE EARTHS  
AND THE ALKALIES.**

\* In separating antimony from the earths and from the alkalies by sulphuretted hydrogen, it is advisable not to add tartaric acid

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<sup>1</sup> The precipitate produced by hydrosulphuret of ammonia in neutral solutions of oxyde of nickel is black, and is not quite insoluble in an excess of the reagent nor in the alkalies. If tartaric acid is present, it cannot be precipitated at all by the alkalies.—Ed.

to the solution, for this acid would prevent the earths from being precipitated by the alkalies. When, therefore, the liquor which has been filtered from the sulphuret of antimony contains tartaric acid, baryta is the only substance which can be accurately determined, because it can be completely precipitated by sulphuric acid. Alumina and magnesia, on the contrary, cannot be precipitated in the slightest degree by the alkalies. When, therefore, the oxydes of antimony have to be separated from the alkalies and from the earths, it is better to add muriatic acid to the solution, in order to render it perfectly clear, or, although the diluted acid liquor be milky, to pass at once a current of sulphuretted hydrogen through it. The liquor having been rendered clear by concentrated muriatic acid, the operator may, if the greatest portion of the antimony have been precipitated in the state of sulphuret of antimony, add the quantity of water necessary to prevent the muriatic acid from acting on the sulphuret of antimony, and then continue the precipitation by sulphuretted hydrogen gas.

DETERMINATION OF THE OXYDES OF ANTIMONY WHEN THEY  
EXIST SIMULTANEOUSLY.

When a liquor contains several oxydes of antimony, the quantities of which have respectively to be determined, the analysis thereof is beset with almost invincible difficulties. If, after having rendered the solution acid, the operator wishes to precipitate the whole of the antimony, by means of sulphuretted hydrogen, for the purpose of estimating from the combinations of antimony and sulphur thus obtained the quantities of oxygen of the oxydes, it is necessary that the liquor should not contain any tartaric acid, for in presence of this acid, a solution which contains antimonious acid, for example, precipitates a sulphuret of antimony, the composition of which is analogous to that of antimonie acid.

Hitherto no method has yet been discovered of accurately



determining the quantities of the various oxydes of antimony when several of them exist simultaneously in solid compounds.

\* When antimonious acid is combined with antimonious acid, the operator might estimate the quantity of the antimonious acid from the volume of oxygen gas which the first of these acids disengages under the influence of a red heat.

## CHAPTER XXXV.

## TUNGSTEN.

## DETERMINATION OF TUNGSTIC ACID.

\* When a solution contains no other fixed base besides tungstic acid, it suffices to evaporate the solution to dryness, and to ignite the dry residuum, after which the quantity of tungstic acid may be at once determined, this acid being absolutely fixed.

\* After ignition the acid is left behind ; it is of a yellowish colour ; if after strong ignition in contact with the air it appears greenish, it is a sign that it is not perfectly pure, and that it contains small quantities of foreign substances. It may be separated by ignition from ammonia, and from all the volatile acids, even from sulphuric acid.

\* When tungstic acid exists in a neutral or in an alkaline solution, it cannot be precipitated by adding an excess of hydrosulphuret of ammonia to the liquor, because the sulphuret of tungsten produced is soluble in this reagent.

\* If a diluted acid is then poured in the solution, a great portion of the tungsten is precipitated, it is true, in the state of sulphuret, of a yellowish-brown colour, but despite of all precautions it is impossible to separate the whole of the metal. The sulphuret produced, however, is very easily converted into pure tungstic acid, by ignition in contact of the air.

\* Neither can tungstic acid be separated completely from its alkaline solution by means of a strong acid. It is precipitated, for the most part, it is true, as a white precipitate, which becomes

yellowish and heavy by the action of heat. When an excess of acid is added, even in evaporating the liquor to dryness, treating the residuum by water and washing it with acidulous water, it is not possible to separate the tungstic acid entirely.

#### SEPARATION OF TUNGSTIC ACID FROM OTHER METALLIC OXYDES.

\* In some cases the determination of tungstic acid is accompanied by numerous difficulties.

\* If the combination of oxyde of tungsten or of tungstic acid with metallic oxydes be in such a state of density that it cannot be easily decomposed by acids, which is the case, for example, with the combination of tungstic acid with protoxyde of iron and protoxyde of manganese found native under the name of ferruginous scheelin,<sup>1</sup> the compound is first reduced into fine powder by levigation, and fused in a platinum crucible with three or four times its weight of carbonate of potash or of soda. The fused mass is then treated by water, which dissolves the tungstate of alkali and the undecomposed carbonate of alkali, leaving a residuum of the oxydes with which the tungstic acid was combined, of course, if these oxydes are insoluble in a solution of carbonate of alkali. After having washed these oxydes, they are to be dissolved in an acid, preferably in muriatic

<sup>1</sup> Ferruginous scheelin, or prismatic wolfram, is essentially a tungstate of iron, and is found in Cornwall, France, Bohemia, Siberia, Greenland, and in Connecticut, as follows :—

	Cumberland.		Haute Vienne in France.	Bohemia.
Tungstic Acid . . . . .	74.666	78.77	73.511	73.60
Protox. of Iron . . . . .	17.594	18.32	20.745	11.20
Protox. of Manganese . . . .	5.640	6.22	5.744	15.75
Silica . . . . .	2.100	1.25	0.000	0.00
	100.000	104.56	100.000	100.55

The two first analyses are by Berzelius, the third by Vauquelin, and the fourth by Richardson.—Ed.

acid, and their quantities are then determined by the methods which have been described before. In such cases tungstic acid can be determined with accuracy only from the loss sustained, because it cannot be completely precipitated from the solution of an alkaline tungstate, either by an acid or by hydrosulphuret of ammonia. If, instead of tungstic acid, the combination contains oxyde of tungsten, the latter would be converted into tungstic acid by fusion with carbonate of alkali.

\* If the oxydes with which tungstic acid or oxyde of tungsten is combined, are not completely insoluble in a solution of carbonate of alkali, they are, for the most part, precipitated in the state of metallic sulphurets when hydrosulphuret of ammonia is poured in the alkaline solution of tungstic acid. This precipitate is collected on a filter, washed with water containing a little hydrosulphuret of ammonia, and then, for the purpose of converting it into oxyde, it is treated by the methods which have been indicated before.

\* *Bisulphate of potash* may be substituted for carbonate of potash to effect the decomposition of this combination. The latter is then to be levigated, and mixed with four parts or five parts of pulverised bisulphate of potash. The mixture is put in a platinum crucible and slowly brought to a low red heat, at which temperature it enters into limpid fusion. The calcining may be effected in a large platinum crucible, by the heat of an argand spirit-lamp. Water is then poured upon the fused mass, by which means the oxydes which were combined with the tungstic acid are dissolved, whilst the tungstic acid remains combined with sulphuric acid and potash. Then, filtering with care the insoluble combination of tungsten, an excess of ammonia is poured upon the whole, which dissolves the latter, whilst the metallic oxydes of the combination are precipitated if insoluble in ammonia. This being done, an excess of hydrosulphuret of ammonia is added to the whole, which dissolves the tungstic acid in the state of persulphuret of

tungsten, and converts the oxydes into metallic sulphurets insoluble in hydrosulphuret of ammonia. They are collected on a filter, washed with water, to which some hydrosulphuret of ammonia has been added. The tungstic acid is determined from the loss.

\* When, on the contrary, a combination of tungstic acid with the metallic oxydes is capable of being decomposed by muriatic acid, or by another acid, all the constituents of the compound can be determined. The compound in this case is reduced to impalpable powder by levigation, and digested with muriatic acid. The greatest part of the tungstic acid separates whilst the other oxydes dissolve in the acid. When the tungstic acid appears perfectly yellowish, and with its peculiar colour, the decomposition is achieved. The acid is collected on a filter, washed, ignited, and its weight is determined. The solution contains the oxydes, with a small quantity of tungstic acid. It is to be rendered ammoniacal, and by means of hydrosulphuret of ammonia, the oxydes are converted into metallic sulphurets, which separate whilst the persulphuret of tungsten remains in solution. These precipitated sulphurets are washed with water containing some hydrosulphuret of ammonia, and they are converted into oxydes in the usual manner. The solution containing the persulphuret of tungsten is evaporated to dryness, and the residuum ignited in contact with the air, by which means it is converted into tungstic acid. The small quantity of tungstic acid thus obtained, added to the previous quantity, constitutes the whole of the acid which existed in the compound.

\* If the compound contained oxyde of tungsten, it is easily converted into tungstic acid when the digestion with the muriatic acid is not effected quite out of the contact of the air.

\* Most of the native compounds containing tungstic acid or oxyde of tungsten, even ferruginous scheelin, are decomposed,

though at times slowly, when left to digest with an acid, when previously reduced to fine powder by levigation.

\* If the operator wishes to determine all the constituents of the compound without excepting the tungstic acid, it cannot be done except by decomposing it by muriatic acid. It is generally preferred, however, to determine only the bases immediately, and estimate the quantity of the tungstic acid from the loss. In that case, it is better to treat the compound by fusion with carbonate of potash; the fused mass is submitted to the action of water, the oxydes remain undissolved, and may be determined in the most exact manner.

\* If a native combination of tungstic acid contained very small quantities of silicic acid, it (the silica) would remain behind after the decomposition by means of an acid, separating the metallic oxydes dissolved by the acid from the undissolved tungstic acid, and then dissolving the latter by ammonia. The silicic acid may thus be collected on a filter, and its quantity determined.

\* It may be readily perceived that these methods are available only for separating from tungstic acid those oxydes the sulphurets of which are insoluble in hydrosulphuret of ammonia; consequently the oxydes of *mercury*, of *silver*, of *copper*, of *uranium*, of *bismuth*, of *lead*, of *cadmium*, of *nickel*, of *cobalt*, of *zinc*, of *iron*, and of *manganese*. As to those oxydes, the metallic sulphurets of which are soluble in hydrosulphuret of ammonia, for example, *peroxyde of tin*, their separation from tungstic acid is attended with difficulties which have not as yet been entirely overcome.

\* Many metallic oxydes may be separated from tungstic acid after digestion in muriatic acid, by evaporating the liquor to dryness, and treating the residuum by alcohol, which dissolves the metallic chlorides which are soluble therein, and leaves the tungstic acid in an insoluble state. The latter may be dissolved

in ammonia, which often leaves a small residuum of a combination of tungstic and of silicic acid. The alcoholic solution of tungstic acid is evaporated to dryness, and the residuum is ignited; the pure acid remains, and its weight is then determined. The metallic chlorides after the volatilisation of the alcohol, are converted into oxydes in the usual manner.

#### SEPARATION OF TUNGSTIC ACID FROM THE EARTHS.

\* In order to separate tungstic acid from the earths, which, like alumina, for example, can be completely precipitated by ammonia, the compound is first decomposed by means of an acid, and the decomposed mass is treated by ammonia, which dissolves the tungstic acid and precipitates the earths. Yet, it is not probable that alumina can thus be completely separated from tungstic acid.

\* Lime, strontia, baryta, may be easily separated from tungstic acid by decomposing the compound by an acid, and leaving the decomposed mass to digest for a considerable time with a solution of carbonate of potash or of soda, heating the whole to ebullition, by which means the earths are precipitated in the state of carbonates, whilst the tungstic acid remains dissolved in the alkaline liquor. If the compound contained a small proportion of silicic acid it would be well, after having decomposed it by an acid, to treat it by an excess of ammonia, which would dissolve all, except the silicic acid; the whole should then be rapidly filtered, in order to prevent any admixture of earthy carbonates to the latter.

\* When the combination of tungstic acid is difficultly decomposable by an acid, it may, after previously reducing it to a very fine powder, be fused in a platinum crucible with three or four times its weight of carbonate of potash or of soda. Treating the fused mass by water, the earth remains in the state of carbonate, whilst the tungstate of alkali and the excess of alkaline carbonate are dissolved by the water. This method is also preferable

to the first for the compounds which are easily decomposable, except that small quantities of silicic acid are then more difficult to separate and to determine.

\*The combinations of tungstic acid with several alkaline earths, principally with lime, known under the name of calcareous scheelin,<sup>1</sup> and which are found in nature, may also be analysed in a manner analogous to that which is employed to separate several metallic acids from tungstic acid (page 308). They are reduced into very fine powder, and decomposed by concentrated nitric or muriatic acid; the decomposed mass is then evaporated to dryness, and the residuum is treated by alcohol, which dissolves the nitrate of lime or the chloride of calcium, and the lime may be precipitated from this solution by sulphuric acid, after which the sulphate of lime produced is washed with weak alcohol. The tungstic acid remains undissolved.

#### SEPARATION OF TUNGSTIC ACID FROM THE ALKALIES.

This analysis presents the greatest difficulties. We have already said, (page 306), that tungstic acid cannot be completely separated from the solutions of the tungstates of alkalies. Sometimes the dry tungstates of alkalies are fused with sulphur, and the product, whilst heated, is exposed to a current of chlorine gas;

<sup>1</sup> Calcareous scheelin, pyramidal tungsten, is essentially a tungstate of lime, and is found principally in Cumberland, Sweden, Bohemia, France, Cornwall, and America. Berzelius gives the following analysis of that found in Sweden :—

Tungstic acid . . . . .	80.42
Lime . . . . .	19.40
	<hr/>
	99.82

That found in Connecticut, according to Bowen, contains—

Tungstic acid . . . . .	76.05
Lime . . . . .	19.36
Oxyde of iron . . . . .	1.03
Silica . . . . .	2.54
	<hr/>
	98.98.—Ed.



red chloride of tungsten is formed, which volatilises, and the alkaline metal remains in the state of chloride. The red chloride of tungsten is dissolved in water, the solution is evaporated to dryness, the residuum is ignited, and tungstic acid remains behind.

\* The combinations of oxyde of tungsten with the alkalies, may be treated in the same manner. If heated in a stream of chlorine gas without previously fusing them with sulphur, they yield a combination of tungstic acid, of chloride of tungsten, and of tungstate of alkali. Wherefore it is necessary to fuse them with sulphur before submitting them to the action of chlorine gas.<sup>1</sup>

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<sup>1</sup> Berzelius saturates the solution of the tungstate of alkali by nitric acid, and decomposes it by subnitrate of mercury; the precipitate produced is calcined, and a residuum of tungstic acid is left.—ED.

## CHAPTER XXXVI.

## MOLYBDENUM.

## DETERMINATION OF MOLYBDENUM AND OF MOLYBDIC ACID.

WHEN molybdic acid exists in solutions, it may, after having diluted them and rendered them acid, be precipitated therefrom by sulphuretted hydrogen in the state of persulphuret of molybdenum which is brown. The first action of this gas is to communicate a blue colour to the liquor, and it is only by passing an excess of the gas that the molybdic acid is pretty completely separated under the form of a brown sulphuret. But the liquor filtered from the precipitate, and above all, the water used for washing it, retains a bluish tinge still. The solutions should be heated, and a current of sulphuretted hydrogen passed through them, which separates a small quantity of brown sulphuret of molybdenum. This operation must be repeated several times in succession, and each time a small quantity of sulphuret is obtained, which must be added to that produced in the first instance. A clear liquor is thus produced at last, from which the aqueous solution of sulphuretted hydrogen can no longer precipitate any sulphuret of molybdenum.

The brown sulphuret of molybdenum produced is collected in a weighed filter, dried with care, and its weight is determined. A known portion thereof is introduced into an apparatus similar to that described (page 128), and treated as for oxyde of cobalt, it is heated by a current of dry hydrogen gas until sulphur ceases to be disengaged, which sulphur is expelled

from the apparatus by means of a small spirit-lamp. The brown sulphuret of molybdenum is thus converted into grey sulphuret of molybdenum ( $\text{MoS}_2$ ) from which the quantity of molybdenum may be calculated by means of the tables.

Molybdic acid may also be precipitated from its neutral or acid solutions. This is done as follows: If the solution is acid, it is first rendered ammoniacal, after which an excess of hydrosulphuret of ammonia is poured in, which the persulphuret of molybdenum produced dissolves. The liquor is left at rest for some time, and it then acquires a golden colour, and after having diluted it with a sufficient quantity of water, muriatic acid is added, and the whole is left at rest until the odour of sulphuretted hydrogen gas disappears. In this manner all the molybdenum is precipitated in the state of sulphuret which is treated by hydrogen gas, as we have just said.

#### SEPARATION OF MOLYBDIC ACID FROM METALLIC OXYDES.

Molybdic acid may be separated from most of the metallic oxydes hitherto treated of, by means of hydrosulphuret of ammonia. The combination of molybdenum is dissolved in an acid, and on this occasion I should say that it is only in a small number of cases that nitric acid is employed for the purpose; the solution is then rendered ammoniacal and put in digestion with an excess of hydrosulphuret of ammonia. The metallic sulphurets which fall down are filtered from the solution of the sulphuret of molybdenum produced, and which is subsequently precipitated from the filtered liquor by muriatic acid.

It is well to employ this method even when the molybdenum is combined with metallic oxydes, which are not susceptible of being precipitated by sulphuretted hydrogen, because the molybdic acid contained in an acid solution is converted, only slowly, into brown sulphuret of molybdenum by sulphuretted hydrogen gas.

\* When the combination of molybdic acid with a metallic

oxyde is difficultly decomposable by acids, it may be fused like the tungstates either with carbonate of potash or of soda, or with bisulphate of potash, by which means it is decomposed. In the first case, by treating the fused mass with water, the metallic oxydes are left as a residuum, provided they be insoluble in a solution of carbonate of alkali, whilst the water dissolves the molybdate of alkali and the excess of carbonate of alkali employed. In the second case, that is, after fusion with bisulphate of potash, the water generally dissolves the whole of the fused mass.

\* When the object in view is the separation of molybdic acid from oxydes, the metallic sulphurets of which are soluble in an excess of hydrosulphuret of ammonia, the separation is attended with difficulties which have not yet been overcome.

#### SEPARATION OF MOLYBDIC ACID FROM EARTHS AND ALKALIES.

When molybdic acid is combined with an alkali or with an earth, the solution may first be treated by hydrosulphuret of ammonia, the sulphuret of molybdenum separated therefrom by muriatic acid, and the alkali or the earth contained in the filtered liquor may then be determined. But the operator may also decompose the salt by nitric acid, and evaporate the whole to dryness; the molybdic acid is thus liberated, and by treating the dry mass by water it remains behind in an insoluble state, whilst the water dissolves the alkaline or earthy nitrate. Molybdic acid may also be separated from lime, strontia and baryta, by digesting for a long time the combination which has been decomposed by an acid with an excess of a solution of carbonate of potash or of soda, which separates the earth in the state of carbonate, whilst the molybdic acid remains dissolved in the alkaline liquor.

\* Perhaps it would be preferable to fuse the combination with an excess of alkaline carbonate, and then to treat the fused mass by water, which would leave the earthy carbonate in an insoluble state, whilst it would dissolve the molybdate of alkali.

## CHAPTER XXXVII.

## VANADIUM.

## DETERMINATION OF VANADIUM AND ITS OXYDES.

\* ACCORDING to Berzelius, vanadium may be quantitatively determined, both in deutoxyde of vanadium (*oxyde vanadique*) and in vanadic acid and their compounds, by igniting them in an atmosphere of hydrogen, by which they are converted into sub-oxyde of vanadium, from the quantity of which that of the metal is calculated.

When vanadic acid is held in solution in a liquor, it may be wholly obtained by evaporation. If the liquor contains volatile acids or ammonia, these substances are dissipated by igniting the residuum in contact with the air. The vanadic acid remains, and its quantity may then be determined. It is necessary to begin by a very moderate heat, which must not be carried on to redness, and the mass, if it contains ammonia, should be stirred, otherwise a little vanadic acid would be reduced into deutoxyde of vanadium (*oxyde vanadique*).

## \* SEPARATION OF VANADIC ACID FROM METALLIC OXYDES.

The oxydes, the metallic sulphurets of which are insoluble in an excess of hydrosulphuret of ammonia, might be separated from vanadic acid by means of this reagent, in the manner which has been described for separating these oxydes from those of antimony, of tungsten, and of molybdenum, as also from

other oxydes which are of an acid nature. The sulphuret of vanadium, dissolved in an excess of hydrosulphuret of ammonia, might then be precipitated by an acid, and should subsequently be washed in the open air until completely converted into vanadic acid.

**\* SEPARATION OF VANADIC ACID FROM PROTOXYDE OF LEAD.**

The protoxyde of lead which is found in nature, combined with vanadic acid, cannot, according to Berzelius, be separated from the latter by ebullition with carbonate of alkali. Wherefore, if the compound contains any arsenic acid or phosphoric acid combined with the protoxyde of lead, the two salts may be separated from the vanadate of lead by boiling the compound first reduced into powder with a solution of carbonate of soda, and evaporating several times the solution to dryness. Water afterwards dissolves the excess of carbonate of soda, and likewise the phosphate and arseniate of soda, whilst the vanadate and carbonate of lead remain in an insoluble state. When the combination contains chloride of lead, the water dissolves the chloride of sodium which has formed.

\* Neither can sulphuric acid separate vanadic acid completely from protoxyde of lead, even after having dissolved the compound in dilute nitric acid. The complete separation can be obtained only by fusing the vanadate of lead with bisulphate of potash. After having treated the fused mass by water there remains a residuum of sulphate of lead, whilst the liquor holds in solution the vanadate of potash produced, and the excess of bisulphate of potash employed.

\* If the vanadate of lead contains chloride of lead, the combination is dissolved in dilute nitric acid, and a solution of nitrate of silver is poured in the liquor, which produces a precipitate of chloride of silver, the quantity of which may then be determined. After filtering, the operator precipitates from the liquor the

excess of nitrate of silver employed, by means of muriatic acid; the filtered liquor is immediately evaporated, sulphuric acid is added towards the end, heat is applied, in order to dissipate completely the muriatic and the nitric acids, and bisulphate of potash is then added. The whole is then fused in a platinum crucible, and the fused mass is treated as we said just now.

\* SEPARATION OF VANADIC ACID FROM BARYTA.

Baryta cannot be separated from vanadic acid by sulphuric acid, not even by adding muriatic acid, or by decomposing the vanadic acid by alcohol. In every case the sulphate of baryta obtained becomes yellow after ignition, and it contains vanadic acid.

\* Baryta can be separated from vanadic acid only by the methods which have been explained for separating it from protoxyde of lead, that is to say, by fusing the combination with bisulphate of potash in a platinum crucible, and treating the fused mass by hot water, which leaves pure sulphate of baryta.

\* SEPARATION OF VANADIC ACID FROM THE FIXED ALKALIES.

According to Berzelius, this separation is difficult to effect. The alkali can hardly in any way be so entirely separated from the muriatic acid, that the latter does not retain any trace of it. The best is to dissolve the vanadate in muriatic acid, to digest the solution with a little sugar until it becomes blue and the vanadic acid is converted into oxyde of vanadium (*oxyde vanadique*), to precipitate the latter by ammonia, and wash the precipitate of vanadite of ammonia with water containing a little ammonia, in which it is insoluble, yet the filtrate retains still a trace of vanadium. It is therefore evaporated, and the dry residuum is ignited until the muriate of ammonia has volatilised; the alkali then remains in the state of metallic chloride.

## CHAPTER XXXVIII.

## CHROMIUM.

## DETERMINATION OF OXYDE OF CHROMIUM.

WHEN chromium exists in the state of green oxyde of chromium in a solution, the best reagent to precipitate it therefrom is ammonia; hydrate of oxyde of chromium is thus obtained, which is to be washed, dried, calcined and weighed. The operator must take some precautions in igniting oxyde of chromium, for, when heated to a certain degree, it suddenly becomes incandescent, owing to which a certain quantity of substance may be lost by projection when the mass is somewhat considerable. Wherefore, it is necessary to calcine the oxyde of chromium in a well closed platinum crucible. Ignition renders it insoluble in acids.<sup>1</sup>

It is necessary, after having precipitated oxyde of chromium by ammonia, to heat the whole a little before collecting it on a filter, or the liquor may be heated well before pouring the ammonia into it, because oxyde of chromium is not precipitated completely from a cold solution. If this precaution be neglected, the filtrate retains still perceptible traces of oxyde of chromium, which impart a slight tinge to it.<sup>2</sup>

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<sup>1</sup> Hydrate of oxyde of chromium at a dark red or red heat, loses completely its water of combination, in which state it forms a dull grass-green powder, and it is then somewhat soluble in acids; to render it completely insoluble it must be strongly ignited, in which state it has a bright grass-green colour.—Ed.

<sup>2</sup> The solution should, in fact, be heated with ammonia until it has become colourless.—Ed.



## DETERMINATION OF CHROMIC ACID.

When chromium exists in a liquor in the state of chromic acid, the operator may, if it is neutral, pour a solution of nitrate of baryta into it, or if it is acid, add a solution of nitrate of lead. Chromate of baryta or of lead is thus precipitated; the latter is insoluble in very dilute acid solutions. The quantity of the chromic acid may be calculated from the weight of the precipitate obtained after ignition. Chromic acid may also be precipitated by pouring a solution of subnitrate of mercury in the liquor previously neutralised. The precipitate of chromate of suboxyde of mercury thus produced is ignited in a platinum crucible, and green oxyde of chromium remains, from the quantity of which that of the chromic acid may be calculated.

A more accurate result, however, is obtained when the chromic acid is reduced into chromic oxyde, directly in the solution; from the weight of the latter, that of the acid may be calculated. The best reagent for reducing chromic acid into oxyde of chromium is muriatic acid. If the liquor is very dilute, it should first be slightly concentrated, and an excess of muriatic acid is added to it; by boiling the whole, the chromic acid is converted into oxyde of chromium, which remains dissolved in the muriatic acid liquor; chlorine is disengaged. This effect, however, takes place only very slowly, and in an incomplete manner; but the reduction is much accelerated, and rendered complete by adding alcohol; this, therefore, should always be done. When alcohol is employed chloric ether is evolved. The whole is then gently heated, in order to volatilise the alcohol, and the oxyde of chromium is precipitated by ammonia.<sup>1</sup>

A current of sulphuretted hydrogen gas may also be passed through the liquor containing the chromate, by which means

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<sup>1</sup> Before precipitating by ammonia, the whole of the alcohol which may still exist in the solution must be expelled by evaporation.—Ed.

the chromic acid is converted into oxyde of chromium, which remains in solution if a free acid has been added to the liquor. Sulphuric acid is formed during the operation, and a great quantity of sulphur is separated, which is collected on a filter after heating the solution in order to dissipate the sulphuretted hydrogen which it contains. Ammonia is then poured in the filtered liquor, which precipitates the oxyde of chromium. The reduction of chromic acid into oxyde of chromium by sulphuretted hydrogen gas, is particularly applicable when the liquor containing the chromate is very dilute. It is necessary, after having passed a current of sulphuretted hydrogen through the liquor, and having completely saturated it, to warm it, and to leave it at rest for a long time, in order that the sulphur may settle well.

\* It is absolutely necessary to add a little free acid to the liquor in which the reduction of chromic acid into oxyde of chromium is effected by sulphuretted hydrogen, for, even an aqueous solution of pure chromic acid is not completely reduced by this gas into oxyde of chromium; but this reduction is most completely effected if muriatic or some other acid has been previously added to the liquor.

\* The separation of oxyde of chromium and of chromic acid from other substances is often difficult, because neither the one nor the other can be precipitated in the state of sulphuret of chromium, either from acid solutions by sulphuretted hydrogen, nor from neutral solutions by hydrosulphuret of ammonia.

SEPARATION OF OXYDE OF CHROMIUM AND OF CHROMIC ACID  
FROM THE OXYDES OF ANTIMONY, OF TIN, OF GOLD, OF PLATINUM,  
OF MERCURY, OF SILVER, OF COPPER, OF BISMUTH,  
OF LEAD, AND OF CADMIUM.

\* It is easy to separate oxyde of chromium and chromic acid from the oxydes which are susceptible of being precipitated from an acid solution by sulphuretted hydrogen. This gas does not exercise any action upon oxyde of chromium, and it

converts chromic acid into oxyde of chromium, which remains dissolved in the liquor. It is hardly possible to calculate the quantity of the metallic oxydes contained in the solution from the weight of the metallic sulphurets obtained, because on account of the conversion of the chromic acid into oxyde of chromium, these sulphurets are thrown down mixed with free sulphur.

\* Oxyde of chromium may also be very readily separated from protoxyde of lead by converting the protoxydes into metallic chlorides by means of muriatic acid, subsequently treating these chlorides by alcohol. Chloride of lead is insoluble in alcohol, whilst the chloride of chromium dissolves therein: ammonia being afterwards poured in this solution precipitates the oxyde of chromium from it. It is necessary to take care to warm the liquor gently beforehand, in order to volatilise the alcohol.

\* When protoxyde of lead is combined with a very small quantity of oxyde of chromium, the separation of the two bodies may be effected by treating the combination with concentrated or dilute sulphuric acid. In the latter case the whole should be evaporated at a gentle heat until the two oxydes have combined with the sulphuric acid, and sulphate of lead has deposited, and the sulphate of chromium has dissolved. Alcohol is then added, in which sulphate of lead is absolutely insoluble, whilst sulphate of chromium may be dissolved therein, especially if the quantity is not very considerable. The sulphate of lead is washed with alcohol, water is added to the alcoholic liquor, and the greater part of the alcohol is to be expelled by heat, after which the oxyde of chromium may be precipitated by ammonia. Yet this method does not answer when the sulphate of chromium has been heated too strongly, and, *a fortiori*, when it has been ignited, for it has then become insoluble in alcohol, and even water does not dissolve it except by a very prolonged contact.

If chromic acid is combined with oxyde of lead, the compound

is boiled with muriatic acid and strong alcohol, by which means the chromic acid is converted into oxyde of chromium under a disengagement of chlor-ether; the oxyde remains dissolved in the muriatic acid, whilst the chloride of lead is insoluble in the spirituous liquor. The chloride of lead is collected upon a weighed filter, washed with alcohol, dried, and when dry weighed. From its weight the quantity of the protoxyde of lead is calculated. This chloride of lead may also be converted into sulphate of lead, from which the quantity of the protoxyde of lead may likewise be calculated.

\* Both the commercial and the native chromate of lead may be very easily analysed by that method. When the chromate of lead of commerce is thus treated, the substances with which it may be mixed, such as sulphate of lime, and sulphate of baryta remain with the chloride of lead in an insoluble state. Before beginning actually to analyse it, it should first be reduced into very fine powder by levigation, because if this precaution be neglected it is not completely decomposed by muriatic acid.

\* When oxyde of silver exists in the acid solutions, muriatic acid is the best reagent for separating from the oxydes of chromium after the treatment of the liquors by sulphuretted hydrogen.

#### SEPARATION OF OXYDE OF CHROMIUM AND CHROMIC ACID FROM THE OXYDES OF NICKEL, OF COBALT, OF ZINC, OF IRON, AND OF MANGANESE.

The separation of these oxydes from oxyde of chromium and chromic acid is difficult. Those which are soluble in an excess of ammonia, like oxyde of zinc, for example, might be separated from oxyde of chromium by means of that alkali, but it is very improbable that their separation might be thus completely effected.

Most of these oxydes, especially peroxide of iron and protoxyde of iron, may be separated from oxyde of chromium by a method similar to that employed for separating zirconia from

94), and titanio acid (page 279), from the oxydes of iron. A sufficient quantity of tartaric acid is added to the solution, which prevents the precipitation of oxyde of chromium and of the oxydes of iron. Hydrosulphuret of ammonia is then poured in the clear ammoniacal liquor, which precipitates sulphuret of iron, whilst this reagent does not exercise any action upon oxyde of chromium, which remains in solution. The liquor is left at rest in a warm place, in order that the sulphuret of iron may settle completely, and the latter is then collected on a filter, washed with water to which some hydrosulphuret of ammonia has been added, and after washing it is converted into peroxyde of iron in the manner described (page 86).

The oxyde of chromium contained in the liquor filtered from the sulphuret of iron has now to be determined, which cannot be done except by evaporating the liquor to dryness, igniting the dry residuum in contact with the air in a counterpoised platinum capsula, until nothing but oxyde of chromium remains. This is best done, as we said (page 94), by introducing the platinum capsula in the muffle of an assay furnace, because it is difficult to burn completely the carbon of the tartaric acid in any other way. If the tartaric acid was pure, the oxyde of chromium obtained is pure also; but if the acid contained lime, which is generally the case with that found in commerce, the whole of this earth remains with the oxyde of chromium.

*Another method* may also be resorted to for separating oxyde of chromium from protoxyde, and peroxyde of iron, and from other oxydes, which cannot be completely dissolved by a solution of carbonate of potash, or of soda. The combination of these oxydes may be fused in a platinum crucible, with an excess of carbonate of potash. The oxyde of chromium, under the influence of the air, passes to a higher degree of oxydisation, as is the case with the oxydes of manganese, and chromate of potash is produced. When the crucible has cooled, the ignited mass is treated by water, which dissolves the chromate of potash produced, and the excess of carbonate of alkali employed, whilst

the peroxyde of iron remains behind, and is collected on a filter. If protoxyde of iron only existed in the liquor, this oxyde absorbs oxygen during the fusion, and remains undissolved in the state of peroxyde of iron. The filtered liquor is acidified by carefully adding muriatic acid thereto, and alcohol being poured in, it is boiled until the chromic acid is converted into oxyde of chromium, which may then be precipitated by ammonia. The peroxyde of iron is dissolved by muriatic acid, and likewise precipitated from the solution by ammonia.

\* In a great number of cases, however, the combination of oxyde of chromium is not completely decomposed by ignition with carbonate of alkali; ordinarily, a small portion only of the oxyde is converted into chromic acid. The conversion of the oxyde of chromium into chromic acid, is much more easily accomplished by fusing the combination with a mixture of alkaline carbonate, and of hydrate of potash. But the most certain way of obtaining it as completely as possible, generally, consists in fusing the combination with a mixture of carbonate, and of nitrate of alkali, until the greater portion of the latter salt is decomposed. The experiment may be made in a platinum crucible. The fused mass is treated by water, and the operator then proceeds as we have just said.

\* Nitrate of potash is preferable to chlorate of potash for this purpose, because the latter is too rapidly decomposed by heat, to permit the complete conversion of the oxyde of chromium into chromic acid, even though the salt be added only little by little at a time to the mass in a state of fusion.

\* The combinations of oxyde of chromium with the oxydes of cobalt, of nickel, and of zinc, may be decomposed in the same manner. The decomposition is effected so much the more rapidly, as the compound operated upon is in a greater state of division.

\* The native combination of oxyde of chromium, and of

protoxyde of iron, called by mineralogists chrome-iron ore,<sup>1</sup> however, is so difficult to decompose, that even after having been reduced into very fine powder by levigation, it is scarcely decomposed by fusion with carbonate of potash. Even though the compound may be fused with a mixture of carbonate, and of hydrate, or of nitrate of alkali, this fusion must be continued for a long time before succeeding in decomposing any notable quantity of the chrome-iron ore.<sup>2</sup> The mass, after fusion, is treated by water, which dissolves the chromate of potash which has formed, the excess of carbonate, or of hydrate of potash employed, and also the, as yet, undecomposed portions of the nitrate of potash. The peroxyde of iron which remains is collected on a filter, well washed, and dissolved in muriatic acid; ordinarily it contains still a portion of undecomposed chrome-iron, even though the fusion may have continued for a very long time, and this quantity remains after the treatment with muriatic acid. This residuum is collected on a filter, its weight is determined, and must be deducted from the quantity of chrome-iron experimented upon. The peroxyde of iron is precipitated by ammonia, and its quantity is determined. The chromic acid of the solution of chromate of potash is now to be converted into

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<sup>1</sup> Chrome-iron is a combination of oxyde of chromium with peroxyde of iron and alumina, in which the oxyde of chromium probably plays the part of an acid. This mineral is found in France in the Department du Var; in Styria in the Gulsen mountains; in Siberia in the Ural mountains; and in North and South America. The analysis of samples from Siberia by Laugier, is as follows:—

Oxyde of Chromium	. . . . .	53.0
Peroxyde of Iron	. . . . .	34.0
Alumina	. . . . .	11.0
Silica	. . . . .	2.0

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100.0

The silica is probably an accidental constituent.—Ed.

<sup>2</sup> This fusion with hydrate and nitrate of potash cannot be performed in a platinum, nor in a silver crucible: a Cornish or Hessian crucible, or one of iron may be used. Care must be taken that the heat applied be intense, examples having occurred of chrome-iron ore having been altogether mistaken for iron-sand of Jameson, and the presence of chrome altogether escaped detection, though especially looked for by some of the most experienced chemists, the mineral having altogether resisted decomposition, for want of a sufficiently high temperature.—Ed.

oxyde of chromium, which is to be precipitated likewise by ammonia.

When chrome-iron ore contains alumina, which is very often the case, this earth is found in the solution of the chromate of potash, provided a sufficient quantity of hydrate of potash has been added to the fused mass; the alumina is then separated by the method which will be indicated farther on.

\* The oxyde of iron which exists in chrome-iron cannot be reduced by hydrogen gas, even with the help of a very strong heat; the degree of oxydisation of the iron contained in this mineral cannot therefore be accurately determined by the method described (page 103.)

\* Chrome iron ore may also be completely decomposed, according to Abich, by exposing it to the highest possible heat in a platinum crucible, with four times its weight of carbonate of baryta.<sup>1</sup>

\* When chromic acid is combined with the oxydes mentioned in this paragraph, the combination is fused with an alkaline carbonate. By treating subsequently the fused mass by water, the oxydes remain undissolved, whilst the water dissolves the chromate of alkali and the excess of alkaline carbonate.

\* SEPARATION OF OXYDE OF CHROMIUM AND CHROMIC ACID  
FROM ALUMINA.

Oxyde of chromium is separated from alumina by means of solution of pure potash, which dissolves the earth and leaves the oxyde; but it is absolutely necessary to boil the two substances for a long time with the solution of potash, because, in the cold,

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<sup>1</sup> The fused mass is then treated as said above; that is to say, the fused mass is treated with dilute muriatic acid at a gentle heat, the solution is evaporated so as to reduce the chromic acid into oxyde of chromium; the mass thus evaporated is redissolved in dilute muriatic acid, and the solution being warmed, ammonia is added, which precipitates the oxyde of chromium, peroxyde of iron, and alumina, which should be filtered out of the contact of the air.—ED.



an excess of the latter dissolves the oxyde of chromium, which is precipitated only by a protracted ebullition. After having separated the oxyde of chromium by filtering, the alumina may be precipitated from the filtrate by supersaturating it with muriatic acid, and adding carbonate of ammonia or pure ammonia thereto.

\* Alumina may be separated from chromic acid by ammonia.

\* It appears, however, that boiling alone with a solution of potash is not sufficient to separate oxyde of chromium completely from alumina, wherefore the precipitated oxyde of chromium should be mixed with an excess of carbonate and of nitrate of alkali, and the whole kept in fusion for a long time, which converts the oxyde into chromate of potash, which is dissolved afterwards by water, whilst the alumina remains. If peroxyde of iron existed at the same time, it would remain likewise in an insoluble state with the alumina.

#### SEPARATION OF OXYDE OF CHROMIUM AND OF CHROMIC ACID FROM MAGNESIA.

Oxyde of chromium is separated from magnesia by fusing both with an excess of alkaline carbonate and of nitrate of potash, and leaving the whole in fusion for a long time. When the fused mass is afterwards treated by water, the chromate of potash formed is dissolved whilst the magnesia remains. The chromic acid contained in the solution is afterwards reduced into oxyde of chromium.

If chromic acid is the substance which is combined with magnesia, the compound is to be fused with alkaline carbonate. When the two substances are contained in a solution, it (the solution) is to be boiled with an excess of carbonate of potash, which precipitates the magnesia.

SEPARATION OF OXYDE OF CHROMIUM AND CHROMIC ACID FROM  
LIME, STRONTIA, AND BARYTA.

\* If oxyde of chromium is contained with these earths in acid solutions, it may be separated therefrom by the same means which are employed to separate peroxyde of iron from lime, strontia, and baryta (page 99). If ammonia is used for the purpose of precipitating the oxyde of chromium from the solution, the precipitate, however carefully the contact of the air may be guarded against, contains a pretty considerable quantity of the alkaline earth, which falls down, not in the state of carbonate, but in that of combination with the oxyde of chromium; for the precipitate does not effervesce with acids.

\* Wherefore, sulphuric acid is employed to separate baryta from oxyde of chromium.

\* When lime is combined with a very small quantity of oxyde of chromium, it may be separated therefrom by decomposing the combination by sulphuric acid, adding alcohol, which produces an insoluble sulphate of lime, whilst the sulphate of chromium dissolves. But the operator must take great care, after treatment by sulphuric acid, not to ignite the mass too strongly, or even not to expel completely the excess of sulphuric acid, for by so doing the sulphate of chromium would not only become insoluble in the alcohol added, but even in pure water.

\* When, on the contrary, lime is combined with a very large quantity of oxyde of chromium, it is much better to fuse the compound with three times its weight of a mixture of alkaline carbonate and of nitrate of alkali. The fused mass is then treated by water, which leaves the lime in the state of carbonate of lime, whilst it dissolves the chromate of alkali, the chromic acid whereof is converted into oxyde of chromium, which may then be precipitated by ammonia.

\* Sulphuric acid may be employed to separate strontia from

oxyde of chromium when contained in a solution, exactly as for baryta, but it is better to follow the process mentioned for separating lime from this oxyde.

\* If the compound to be analysed is a combination of chromic acid with these three earths, it must be fused with an alkaline carbonate; the fused mass is treated by water, which leaves the earths in the state of insoluble carbonates. Chromate of baryta may also be decomposed by reducing it into very fine powder, and treating it by muriatic acid and alcohol. The chromic acid is thereby converted into oxyde of chromium, which remains dissolved in the muriatic acid as well as the baryta; the latter is then precipitated by sulphuric acid, and the oxyde of chromium by ammonia.

\* If the earthy chromates are combined, or exist in conjunction with earthy sulphates, the compound should be treated by muriatic acid and alcohol, as we have just said, and the earthy sulphates remain in an insoluble state at the bottom of the alcoholic liquor.

#### SEPARATION OF OXYDE OF CHROMIUM AND CHROMIC ACID FROM THE ALKALIES.

Oxyde of chromium is separated from the alkalies in the same manner as peroxyde of iron is separated from these substances, by means of ammonia (page 99). The best way of analysing the combinations of chromic acid with the alkalies consists in treating them by water, so as to obtain concentrated solutions; the chromic acid is converted into oxyde of chromium by means of muriatic acid and alcohol, the liquor is then heated in order to dissipate the alcohol, the oxyde of chromium is precipitated by ammonia, and the alkali contained in the filtered liquor is determined in the state of metallic chloride.

DETERMINATION OF OXYDE OF CHROMIUM AND CHROMIC ACID  
WHEN THEY EXIST SIMULTANEOUSLY.

When oxyde of chromium and chromic acid have to be separated from each other, and both are in the state of solution, the following process may be followed, according to Maus:— A solution of acetate of lead is added to the liquor, which produces a precipitate of chromate of lead, whilst the oxyde of chromium and the excess of acetate of lead employed remain in solution. Yet it is necessary that the liquor should not contain enough free acid to retain a little chromate of lead in solution. An excess of acetic acid is not objectionable, because chromate of oxyde of chromium is insoluble in this acid.

If the operator has to analyse a solid compound of chromic acid and oxyde of chromium which has been recently precipitated, it may be digested with a solution of acetate of lead, to which a little free acetic acid has been added. The oxyde of chromium is thus obtained in solution, whilst the chromate of lead remains insoluble; sulphuretted hydrogen is then passed through the solution of the oxyde of chromium, in order to remove the oxyde of lead in excess, and the oxyde of chromium may afterwards be precipitated. It is advisable also to decompose the chromate of lead, in order to ascertain the quantity of chromic acid which it contains; this is best done by means of muriatic acid and alcohol. The chloride of lead produced is separated, and the quantity of oxyde of chromium in the filtered liquor is determined, from which that of the chromic acid may be estimated.

## CHAPTER XXXIX.

## ARSENIC.

## DETERMINATION OF ARSENIC, OF ARSENIUS, AND OF ARSENIC ACIDS.

VARIOUS methods may be resorted to for the quantitative determination of the arsenious and arsenic acids contained in a solution. If the liquor, besides arsenic acid, contains nitric acid only, and no fixed substances, it is mixed with a most exactly weighed quantity of pure protoxyde of lead which has just been ignited; it is then evaporated to dryness, and the residuum is then ignited in a small counterpoised platinum capsula. The quantity of the arsenic acid is determined by deducting the weight of the protoxyde of lead employed from that of the calcined mass. But it is necessary that the arsenic acid should not be accompanied in the solution by any other acid capable of producing with the protoxyde of lead a salt which can resist the action of the fire. The presence of ammonia is likewise objectionable in this method of analysis.

\* If the liquor contains any arsenious acid, nitric acid is added, and likewise a weighed quantity of protoxyde of lead; the whole is then evaporated, the residuum is ignited; it consists of arsenic acid and protoxyde of lead. From the quantity of arsenic acid that of the arsenious acid is calculated. When arsenious acid and nitrate of lead are calcined together, the first of these substances is completely converted into arsenic acid.

wash, on account of the presence of nitric acid in the solution. The collective quantities of sulphur indicate that which existed in the sulphuret of arsenic subjected to analysis; the loss indicates that of the arsenic from which the proportion of the arsenious acid is calculated.

It is necessary to take care, in this operation, to collect the undissolved sulphur only after a prolonged digestion in aqua regia. The colour of sulphuret of arsenic does not differ much from that of sulphur; yet a little practice enables the operator to detect very readily whether the sulphur contains sulpharsenious acid or not.

\* When arsenious acid has been precipitated from a liquor, by means of sulphuretted hydrogen, and its weight has been determined, the small quantity of sulphur mixed with the sulphuret may often be separated by means of ammonia, which dissolves the sulphuret, and leaves the sulphur quite untouched, and the quantity of which may, therefore, be then easily determined. The whole of the sulphur cannot, however, be entirely obtained, a portion remaining dissolved in the ammoniacal solution of the sulpharsenious acid.

Arsenic acid may be quantitatively determined in a solution, in the same manner as for the determination of arsenious acid, that is to say, by means of sulphuretted hydrogen, when the use of protoxyde of lead is not practicable, as for example, when the liquor contains muriatic acid, or fixed substances. But arsenic acid is precipitated by sulphuretted hydrogen much more slowly than arsenious acid. This precipitation requires much more time than that of any other substances whatever by sulphuretted hydrogen. The quantity of sulphuret of arsenic produced, which remains dissolved in the liquor saturated with sulphuretted hydrogen, is also much more considerable than is the case with arsenious acid. The last traces may, however, be precipitated by digesting the whole at a very gentle heat, until the odour of sulphuretted hydrogen has disappeared.

\* There is no metallic oxyde, the precipitation of which by sulphuretted hydrogen requires so much precaution as arsenic acid. Even when the operator thinks that he has completely precipitated the sulphuret of arsenic, it is necessary to take a portion of the filtered liquor, and to add thereto its own volume of aqueous solution of sulphuretted hydrogen. The whole is then left at rest in an open vessel, in order to ascertain whether after a certain time a slight precipitate of sulphuret of arsenic will not appear.

If the operator knows positively that the solution contains arsenic acid alone, the quantity of this acid might be calculated from the sulphuret produced; this sulphuret is a persulphuret of arsenic (sulpharsenic acid), the composition of which corresponds to arsenic acid; yet the operator must not forget that the sulphuret precipitated in this case contains an excess of sulphur produced by the action of the air upon the sulphuretted hydrogen dissolved in the liquor. And, as this excess of sulphur may often amount to some per cents, it is necessary to analyse this sulphuret, which is done in the same manner as for sulpharsenious acid, that is to say, for the sulphuret of arsenic, which is precipitated from the solution of arsenious acid by sulphuretted hydrogen.

Instead of passing a current of sulphuretted hydrogen through the dilute solution, for the purpose of determining the quantity of arsenious or of arsenic acid contained therein, the following method may be adopted:—The acid liquor is supersaturated with ammonia, and a quantity of hydrosulphuret of ammonia is added thereto, which produces a precipitate of sulphuret of arsenic, which dissolves easily and completely in the excess of hydrosulphuret of ammonia, whatever be its degree of sulphuration; that is to say, whether it be sulpharsenious or sulpharsenic acid. If the solution is very concentrated, it should be diluted with a large quantity of water, and muriatic acid is carefully added to it, so as to render it slightly acid. Sulphuret of arsenic is thereby precipitated under disengagement of sulphuretted

hydrogen. The liquor is digested at a gentle heat, until the odour of sulphuretted hydrogen has vanished, and the sulphuret of arsenic produced is separated by filtering. It is absolutely necessary to analyse this sulphuret, as we have said, because it is mixed with much sulphur from the decomposition of the hydrosulphuret of ammonia.

\* This method is preferable to that mentioned before, at least for the determination of arsenic acid, for the latter is thus much more completely precipitated in the state of sulphuret of arsenic.

\* If, when this method is resorted to, the operator has not added a very large quantity of water to the solution of the sulphuret of arsenic in hydrosulphuret of ammonia before decomposing it by muriatic acid, and too large a proportion of this acid is subsequently added, the whole of the arsenic is not obtained in the state of sulphuret. It is better, in a great number of cases, to decompose the liquor with acetic acid instead of with muriatic acid.

The method, which consists in precipitating arsenious and arsenic acids in the state of sulphurets of arsenic, and in determining, from the sulphuret thus obtained, the quantity of metallic arsenic, is almost the only one (except that of Berthier, of which we shall speak presently), which yields satisfactory results. Ordinarily, arsenic acid is precipitated by a solution of acetate or of nitrate of lead in the state of arseniate of lead, from the weight of which the quantity of the arsenic acid is determined; but this method is seldom satisfactory, and is besides attended with more difficulties than that which has just been described, when the solution contains other metallic oxydes. It is also necessary to determine the quantity of the arsenic acid in the arseniate of lead produced, in order to obtain anything like tolerable accuracy; this method is much more complicated than the quantitative determination of arsenic in the state of sulphate.

\* Berthier has indicated *another method* of determining



arsenic acid quantitatively in solutions which may contain not only nitric and muriatic acid, but likewise sulphuric acid, and even certain fixed substances. It is as follows:—Take a certain weight of pure metallic iron, dissolve it in hot nitric acid, mix this solution of peroxyde of iron with the liquor in which arsenic acid has to be determined, and precipitate the whole by an excess of ammonia. If the quantity of peroxyde of iron added is sufficient to form a basic salt with the arsenic acid, this acid is thereby completely precipitated, because arseniate of sesquioxide of iron is neither dissolved nor decomposed by ammonia. The precipitate is very mucilaginous and difficult to wash. Yet when a large excess of peroxyde of iron has been employed, the precipitate is more bulky, it is true, but it may be washed more rapidly, because the precipitate is less mucilaginous in proportion, and suffers the liquor and the water used for washing it to percolate more readily. After drying, the precipitate is ignited. At first the heat applied must be very gentle, because the precipitate contains a little ammonia, which is thus volatilised. Were the operator to act otherwise, and at once apply a strong heat, a little arsenic acid might be reduced into arsenious acid by the ammonia, and be lost. If the liquor contains sulphuric acid, it is advisable, after having ignited and weighed the precipitate, to calcine it a second time, in order to see whether it loses weight thereby; for it might happen that a portion of sulphuric acid should have escaped volatilisation from the heat not having been applied long enough.

\* From the weight of the calcined precipitate, the quantity of arsenic acid in the solution is found, for the surplus weight of the peroxyde of iron consists in arsenic acid. As the quantity of the iron dissolved is known, that of the peroxyde of iron is of course known also. Yet it must not be forgotten that every species of forged iron contains a little carbon which, it may be admitted, amounts to one half per cent. in ordinary forged iron, and 100 parts of which consequently yield only 143.50 of peroxyde of iron instead of 144.22.

\* This method must not be employed when the liquor, besides

arsenic acid, contains metallic oxydes, even when these are not precipitable by an excess of ammonia; neither must it contain lime, strontia, nor baryta. The alkalies are about the only fixed substances the presence of which is not detrimental.

\* It is necessary to add peroxyde of iron in sufficient quantity, because the neutral arseniate of sesquioxide of iron is soluble in ammonia. A large excess of this oxyde, on the contrary, is advantageous, as I have remarked before. The proportions to be employed, however, are about one part of iron for two parts of the arsenic acid suspected to exist in the liquor.

\* This method may serve likewise to determine the quantity of arsenious acid in the liquor, after it has been converted into arsenic acid by aqua regia.

\* Berthier's process can be recommended only in certain special cases. Very frequently the whole of the arsenic acid is not precipitated by ammonia, a small portion of which remains dissolved, especially when a large quantity of the reagent has been employed. It is therefore better, in most cases, to determine arsenic acid by sulphuretted hydrogen or by hydrosulphuret of ammonia.

SEPARATION OF ARSENIUS AND ARSENIC ACIDS FROM THE  
OXYDES OF CHROMIUM, OF TITANIUM, OF URANIUM, OF  
NICKEL, OF COBALT, OF ZINC, OF IRON, AND OF MANGANESE,  
FROM THE EARTHS AND FROM THE ALKALIES.

These substances not being susceptible of precipitation by sulphuretted hydrogen, this reagent is employed to separate them from arsenious and from arsenic acids. The dilute solution should first be acidified, preferably in most cases by muriatic acid, and a current of sulphuretted hydrogen is passed through it to complete saturation; it is then left at rest at a very gentle heat, until it no longer exhales the odour of sulphuretted hydrogen. The sulphuret of arsenic which has precipitated is collected on a filter, and determined in the manner which has been described before; the other substances are afterwards

separated from the filtered liquor. If the solution contained any peroxyde of iron the sulphuretted hydrogen gas will have converted it into protoxyde of iron.

If metallic arsenic is alloyed to the metals of the oxydes mentioned in the title of this paragraph, the alloy is to be dissolved in nitric acid or in aqua regia; the solution is diluted by water, and treated by sulphuretted hydrogen. In this case the treatment of the alloy by nitric acid is sometimes preferable to that by aqua regia, because nitric acid converts it principally into arsenious acid, whilst aqua regia produces chiefly arsenic acid which is precipitated by sulphuretted hydrogen with more difficulty than the other. When the arsenical alloy has been dissolved in hot nitric acid, the solution must be diluted by water whilst it is still hot, otherwise the arsenious acid would crystallise on cooling. In general, the use of nitric acid is inconvenient, because it dissolves arsenious acid too sparingly; wherefore, when the metallic compound contains much arsenic, a portion of the arsenious acid crystallises in the liquor, and shelters the, as yet, undecomposed portions from the action of the acid. In such cases aqua regia must be resorted to.

\* When metallic arsenic is combined with metals which cannot be precipitated from acid solutions by sulphuretted hydrogen in the state of sulphuret, as for example, iron, nickel, cobalt, zinc, manganese, and the combination contains at the same time traces of copper, of bismuth, or of another metal which, like arsenic, is precipitated from an acid solution in the state of sulphuret by sulphuretted hydrogen, the best is to dilute the acid liquor by water, and to pass for a very short time a current of sulphuretted hydrogen through it, or to add a little hydro-sulphuret of ammonia; the small portion of sulphuret of copper, of sulphuret of bismuth, &c., is thus precipitated in combination with a little sulphuret of arsenic. This precipitate is collected on a filter, and is immediately treated with the filter by aqua regia or nitric acid, which dissolves it, leaving at times a small proportion of sulphur; the solution is saturated by ammonia, and

DETERMINATION OF OXYDE OF CHROMIUM AND CHROMIC ACID  
WHEN THEY EXIST SIMULTANEOUSLY.

When oxyde of chromium and chromic acid have to be separated from each other, and both are in the state of solution, the following process may be followed, according to Maus:— A solution of acetate of lead is added to the liquor, which produces a precipitate of chromate of lead, whilst the oxyde of chromium and the excess of acetate of lead employed remain in solution. Yet it is necessary that the liquor should not contain enough free acid to retain a little chromate of lead in solution. An excess of acetic acid is not objectionable, because chromate of oxyde of chromium is insoluble in this acid.

If the operator has to analyse a solid compound of chromic acid and oxyde of chromium which has been recently precipitated, it may be digested with a solution of acetate of lead, to which a little free acetic acid has been added. The oxyde of chromium is thus obtained in solution, whilst the chromate of lead remains insoluble; sulphuretted hydrogen is then passed through the solution of the oxyde of chromium, in order to remove the oxyde of lead in excess, and the oxyde of chromium may afterwards be precipitated. It is advisable also to decompose the chromate of lead, in order to ascertain the quantity of chromic acid which it contains; this is best done by means of muriatic acid and alcohol. The chloride of lead produced is separated, and the quantity of oxyde of chromium in the filtered liquor is determined, from which that of the chromic acid may be estimated.

## CHAPTER XXXIX.

## ARSENIC.

## DETERMINATION OF ARSENIC, OF ARSENIUS, AND OF ARSENIC ACIDS.

VARIOUS methods may be resorted to for the quantitative determination of the arsenious and arsenic acids contained in a solution. If the liquor, besides arsenic acid, contains nitric acid only, and no fixed substances, it is mixed with a most exactly weighed quantity of pure protoxyde of lead which has just been ignited; it is then evaporated to dryness, and the residuum is then ignited in a small counterpoised platinum capsula. The quantity of the arsenic acid is determined by deducting the weight of the protoxyde of lead employed from that of the calcined mass. But it is necessary that the arsenic acid should not be accompanied in the solution by any other acid capable of producing with the protoxyde of lead a salt which can resist the action of the fire. The presence of ammonia is likewise objectionable in this method of analysis.

\* If the liquor contains any arsenious acid, nitric acid is added, and likewise a weighed quantity of protoxyde of lead; the whole is then evaporated, the residuum is ignited; it consists of arsenic acid and protoxyde of lead. From the quantity of arsenic acid that of the arsenious acid is calculated. When arsenious acid and nitrate of lead are calcined together, the first of these substances is completely converted into arsenic acid.

\* The arseniate of lead then obtained must not be ignited too strongly, but only heated to incipient redness, for a stronger heat might expel a small proportion of arsenic acid in the state of arsenious acid and of oxygen.

It is not easy to convert arsenious into arsenic acid by means of nitric acid; aqua regia alone answers the purpose; and if the solution is too dilute it should be concentrated.

When the solution from which arsenious acid has to be separated contains muriatic acid, the quantity of the first of these acids cannot be determined by means of protoxyde of lead, in the manner which has been described. In this case, and in general when the liquor contains other substances which preclude the use of the mode of analysis by protoxyde of lead, the arsenious acid may be determined by passing a current of sulphuretted hydrogen through the acid solution. If the liquor be dilute, a precipitate of sesquisulphuret of arsenic (sulpharsenious acid) is produced, the composition of which corresponds to that of arsenious acid. The stream of sulphuretted hydrogen is continued until the liquor is completely saturated; the whole is then left at rest in a very moderately warm place, until the odour of sulphuretted hydrogen has vanished. The last traces of sulphuret of arsenic are thereby precipitated.

\* When the aqueous liquor from which arsenious acid has to be precipitated by means of sulphuretted hydrogen is dilute, it is necessary to add muriatic acid to it.

\* A small portion of the precipitated sulphuret of arsenic adheres so strongly to the side of the vessel and of the glass tube which plunges in the liquor, that it cannot be removed by mechanical means, but it is very easily dissolved by a few drops of ammonia; this solution is added to the acid liquor, which precipitates the small quantity of dissolved sulphuret of arsenic. If the liquor contains any oxyde of cobalt, a solution of carbonate of soda must be employed instead of ammonia, for the purpose of dissolving the small quantity of sulphuret of arsenic just

mentioned, because oxyde of cobalt cannot be precipitated completely by potash from a solution which contains ammonia.

The sulphuret of arsenic obtained is collected upon a weighed filter, washed, dried at a very gentle heat, and then weighed. Were the operator quite sure that the solution contains arsenious acid only, he might calculate the quantity of this acid from that of the sulphuret of arsenic produced, though even in that case the result would be erroneous, because the sulphuret contains more sulphur than is found by calculation, because it is mixed with a little sulphur, due to the decomposition of the excess of sulphuretted hydrogen in the liquor. But whenever it is presumed that the solution contains a little arsenic acid, besides arsenious acid, the sulphuret of arsenic obtained must absolutely be analysed, which, for the reason just related, should always be done, even when the liquor contains arsenious acid only. The best method of performing this analysis, is the following :—

After having dried and weighed the sulphuret of arsenic, all that which can be shaken from the filter is put into a small matrass, or a large glass vessel, and the filter is again weighed, in order to know the amount of substance submitted to experiment. Aqua regia is then poured upon it, and the whole left to digest for some time. The action of the acid upon sulphuret of arsenic in very fine powder, is very energetic, even in the cold, owing to which the oxydisation must be performed in capacious vessels. The arsenic is converted into arsenic acid, a portion of the sulphur is converted into sulphuric acid, and the other remains in the pure state. In order to convert the whole of the sulphur into sulphuric acid, the digestion in aqua regia, which should be frequently renewed, would require too long a time. Wherefore, as soon as the sulphur is agglomerated into small lumps, it is collected upon a weighed filter, washed, dried most carefully, and then weighed. A solution of chloride of barium is added to the filtered liquor, and from the quantity of the sulphate of baryta obtained, that of the sulphur in solution is calculated. The sulphate of baryta is very difficult to

contains it in nitric acid, adding afterwards to the liquor a solution of nitrate of lead, and cautiously evaporating the whole to dryness; the excess of nitric acid is thus volatilised, and the water by which the dry mass is treated, dissolves only the excess of nitrate of lead and the bases primitively combined with the arsenic acid, whilst an insoluble residuum of arseniate of lead remains behind, from the weight of which the quantity of the arsenic may be calculated, in doing which the salt is generally considered as being neutral. This supposition, however, is not exact, and it is at least necessary to determine the quantity of oxyde of lead contained in the arseniate of lead obtained. The operator should also, in order to determine the quantity of the base, separate from the filtered liquor the protoxyde of lead which it may hold in solution. From that which we have said, it may be seen that, as we remarked at the beginning, this method is not to be recommended.

SEPARATION OF ARSENIC AND ARSENIOS ACID FROM PROTOXYDE  
OF LEAD, BARYTA, STRONTIA, AND LIME.

The bases with which sulphuric acid forms compounds which are insoluble in water or in weak alcohol, may be separated from arsenic acid, and the quantity determined by a method at once accurate and easy. These bases are baryta, lime, strontia, and protoxyde of lead. When the bases are combined with arsenic acid, and the compound to be analysed is in the solid state, its weight is first determined. If it contains water, it should be ignited before weighing, it is then pulverised, and sulphuric acid is poured upon it, with which it is left to digest for some time. If the base consists of baryta alone, water is added; the sulphate of baryta produced is collected on a filter, washed, and its weight is determined, from which the quantity of the baryta is calculated. That of the arsenic acid is also very accurately ascertained from the loss. If the base is lime, strontia, or protoxyde of lead, after having decomposed the combination by sulphuric acid, instead of water, alcohol is



added, in which the sulphates of these bases are insoluble, whilst the arsenic acid liberated and the excess of sulphuric acid added dissolve therein. The sulphates are separated by filtering, they are washed with alcohol, and their weight is determined, from which the quantity of the bases is calculated.

\* That of the arsenic acid is estimated from the loss. As their bases may be determined with a great accuracy in the state of sulphates, it is only in a small number of cases that arsenic acid has to be determined in the liquor filtered from the sulphates, especially when this liquor contains alcohol.

However, before digesting these combinations of arsenic acid with sulphuric acid, it is advisable to treat them by muriatic acid, in which the neutral and basic arseniates are all soluble; the acid arseniates dissolve also therein, but only when they are dry. Most of the acid arseniates whose base is an earth or a metallic oxyde, are not dissolved by concentrated muriatic acid after ignition, and can be decomposed only by boiling their powder with concentrated sulphuric acid in a porcelain capsula for a long time, but not so as to volatilise all the sulphuric acid. After cooling, if water be poured on the mass, it dissolves it completely, provided the base is not, of course, one of those which form with sulphuric acid compounds which are insoluble or sparingly soluble in this menstruum.

\* The combinations of arsenious acid with protoxyde of lead, baryta, strontia, and lime, may be likewise analysed with great precision. After drying, they are weighed, preferably in a small counterpoised platinum crucible or capsula, and pure nitric acid of ordinary strength is poured upon it. The whole is evaporated at a very gentle heat without boiling the acid, the dry residuum is then heated to incipient redness and it is weighed. The ignition and weighing may be repeated in order to see whether the weight of the oxydised mass remains uniform. By heating it too strongly some arsenic may be disengaged, and reduced into arsenious acid and oxygen. The ignited product is decomposed, as we have said, by muriatic and sulphuric acids.

After having weighed the earthy sulphate, all the constituents of the arsenious compound may be determined, even the proportion of the water which exists in all arsenites. The weight of the earthy sulphate gives the quantity of the base, and deducting it from that of the ignited mass, the operator may know how much arsenic acid the said mass contained, from which the quantity of arsenious acid in the compound may be calculated. The quantity of the arsenite experimented upon, which exceeds that of the base and of the calculated arsenious acid, consists of water.

#### SEPARATION OF ARSENIC FROM ITS ALLOYS WITH OTHER METALS.

When the compound to be analysed is an alloy of arsenic with other metals, most of the latter may be separated from the arsenic by means of chlorine gas, according to the method described (page 298) for separating antimony from the metals, the chlorides of which are not volatile. Metallic arseniurets, however, are far from being as easily decomposed by chlorine as the combinations produced by the union of the sulphurets of arsenic and of antimony with other metallic sulphurets; and the method of decomposing such compounds by chlorine will be described farther on, in the article SULPHUR. Some of these alloys are of such a nature, that even when operating upon a few *grammes* only, and though chlorine gas may have been passed over the heated alloy for a whole day, yet a portion remains still in the bulb in an undecomposed state; consequently, when the non-volatile chlorides are afterwards treated by water, for the purpose of dissolving them if soluble, a residuum is left, which consists in the portion which has escaped decomposition. This residuum must be weighed, and its weight deducted from that of the quantity of the substance experimented upon. On account of the slow heat with which metallic arseniurets are decomposed, this method of analysing them, by means of chlorine gas, should be resorted to only when the metallic oxydes cannot be separated from the acids of arsenic by the sulphuretted hydrogen, nor by hydrosulphuret of ammonia. If it is possible to separate them

by one or the other of these reagents, the metallic arseniurets should be dissolved in nitric acid or in aqua regia.

#### SEPARATION OF METALLIC ARSENIC FROM TIN.

The separation of metallic arsenic from tin is attended with difficulties which have not yet been overcome. No accurate method has hitherto been discovered of separating these two metals.<sup>1</sup>

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<sup>1</sup> Among the methods which have been proposed for this object is the following, which consists in converting both metals into sulphurets, and passing a stream of hydrogen over them, heat being applied at the same time, by which means both sulphurets are reduced, and the arsenic is taken up by the hydrogen. In the monthly "Comptes Rendus" of the Academy of Berlin for May, 1847, M. Rose proposed the following method for separating tin from antimony, as follows: Concentrated muriatic acid is poured upon the metals, when the violent oxydisation produced is completed, the mass is evaporated at a gentle heat, the dry powder of the oxydes is fused in a silver crucible with an excess of caustic soda. The fused mass is softened by treatment with a very large quantity of water, heat is applied, and after complete cooling the antimoniate of soda is thrown upon a filter and washed with a dilute solution of carbonate of soda. It is dissolved, whilst still moist, in a mixture of tartaric and of muriatic acid, and the antimony is precipitated by sulphuretted hydrogen. The solution of stannate of soda is also acidified by muriatic acid, and the tin may be precipitated also in the state of sulphuret. H. Rose has, however, published quite recently a new process for the estimation of arsenic, antimony, and tin, which we reproduce here as it appeared in the "Chemical Gazette:"—

"Chloride of ammonium can be usefully employed in analytical investigations from its property of decomposing several oxydes at a high temperature, and forming with the metals highly volatile chlorides. The experiments frequently give far more accurate results, in the shortest time and with the least trouble, than have hitherto been obtained by the usual methods of analysis.

"It is well known what difficulties accompany the separation of the acids of arsenic and of antimony, as likewise that of the peroxyde of tin, from bases. In general, these metallic acids are separated from the solutions of most of their salts in hydrochloric acid, or to which hydrochloric acid has been added, by sulphuretted hydrogen, as sulphurets, and the base in the filtered liquid determined in the state of chloride. If the latter happens to be one which is easily decomposed at an elevated temperature, and not volatile or only so at a very high temperature, the liquid, which is frequently very considerable in quantity, has to be evaporated to dryness, and the residue ignited more or less strongly. Every one accustomed to analytical investigations must be sufficiently well acquainted with the inconveniences which accompany the evaporation of large quantities of liquids containing small amounts of alkaline salts which have to be determined quantitatively.

"The difficulties attending such an investigation become greater when the salt of the metallic acid is not at all, or very sparingly, soluble in water and in hydrochloric

## SEPARATION OF ARSENIC FROM ANTIMONY.

The separation of metallic arsenic from antimony is also attended with numerous difficulties, yet if the two metals are

acid, or one which is easily decomposed. Now, this is frequently the case with a salt of this class when it has been heated to redness, which is requisite in determining the amount of water directly.

"All these difficulties may in many cases be avoided by the use of chloride of ammonium. Suppose we have a salt of one of these metallic acids with an alkaline base to examine, it is only requisite to mix it, after having ignited and weighed it in the finely-pulverised state, with from five to eight times the quantity of pure powdered chloride of ammonium, and to heat the mixture in a small porcelain crucible, which may be covered with a concave platinum lid, over an argand lamp, until the whole of the chloride of ammonium is volatilised. The alkali is left behind in the state of chloride, the quantity of which may be very accurately determined. So long as chloride of ammonium is volatilised the temperature is so low that none of the alkaline chloride can escape. As soon as the ammoniacal salt is driven off, the temperature is moderated, so that the residue in the porcelain crucible does not fuse. After weighing it is mixed with a fresh quantity of chloride of ammonium and again heated, in order to see whether the weight of the residue remains constant or is diminished, in which latter case the treatment with chloride of ammonium must be repeated. Sometimes, owing to the access of air, the platinum lid is coated with a film of the metallic acid, especially with peroxyde of tin, when stannates are examined. In this case the lid, in the subsequent ignition, is covered with a little of the ammoniacal salt.

"I will here describe some experiments which have been made by M. Weber :—0·609 grm. of ignited arseniate of soda,  $2\text{NaO} + \text{AsO}_5$ , afforded, after being once treated with five times the amount of chloride of ammonium, 0·455 grm. chloride of sodium. The weight remained the same after repeating the treatment with chloride of ammonium. The quantity of chloride of sodium corresponds to 35·46 per cent. soda in the salt ; the theoretical quantity is 35·18.

1·948 grm. antimoniate of soda ( $\text{NaO SbO}_5 + 7\text{HO}$ ), the amount of soda in which, according to Frémy's analysis, is 11·9 per cent., afforded, after five ignitions with chloride of ammonium, a constant weight of 0·429 grm. chloride of sodium, which corresponds to 12·58 per cent. of soda ; the salt had been dried for a length of time at  $212^\circ$ , and it is possible that it had lost some of its water of crystallisation.

"*Stannate of Potash*.—This salt had been precipitated by alcohol from the solution of the peroxyde of tin in hydrate of potash, washed with alcohol, then dissolved in water and evaporated. It formed, after drying under the air-pump over sulphuric acid, a gummy mass, which again easily dissolved in water ; it contained the *b*-modification of the oxyde of tin. According to an examination after the usual method, the salt dried at  $212^\circ$  consisted, in 100 parts of—

87·34 peroxyde of tin . . . . .	18·67 oxygen.
8·02 potash . . . . .	1·35 "
4·64 water . . . . .	4·11 "

combined together in the reguline state, it suffices to heat the alloy out of the contact of the air, in order to volatilise the arsenic which distils over. This method is not applicable when arsenic has to be separated from other metals, because at a red heat the metals ordinarily retain a portion, and sometimes even the whole of the arsenic, which it is not even possible to dissipate in any thing like a complete manner by roasting in the free air.

When antimony has to be separated from arsenic, the best is to heat the alloy to redness in an atmosphere of hydrogen gas. For this purpose an apparatus may be employed similar to that represented (page 128). When the quantity of arsenic is considerable, it is necessary that the diameter of the tube soldered to the farther side of the glass bulb *g* be not too small. As soon as the apparatus is filled with hydrogen gas, the bulb *g* is heated, and the heat is continued until no more metallic arsenic is deposited in this farther tube. By means of a small spirit-lamp the metal is constantly expelled from the tube until it (the tube) remains clear. When the arsenic has been completely expelled from the tube, the glass bulb is suffered to cool, but without interrupting the current of hydrogen. It is then weighed with the residuum of metallic antimony, and the loss indicates the quantity of arsenic. It is necessary in this operation not to employ too strong a heat, which would volatilise a little the antimony. Of course, it is hardly necessary to add, that the operator should take great care not to inhale the arsenical vapours, wherefore the experiment must be conducted not in the laboratory, but under the hood of the furnace opening in the chimney-flue. Nearly all the arsenic found in nature, under

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According to this the composition of the salt is  $\text{KH} + 7\text{SnO}^2 + 3\text{HO}$ . The acid metastannate of potash is, according to Frémy,  $\text{KO} + 6\text{SnO}^2 + 5\text{HO}$ . It is possible, therefore, that the salt prepared by me contained a quantity of a still more acid salt mixed with it.

“Of the salt used for the above analysis, 1·013 grm. was mixed with five times the amount of chloride of ammonium and heated to redness; this was repeated twice with smaller quantities of chloride of ammonium, when the weight of the residue no longer varied; 0·131 grm. chloride of potassium was obtained, corresponding to 8·09 per cent. of potash. All the chlorides obtained dissolved entirely in water, and when tested did not exhibit the least trace of the metallic acids.”

the name of "native arsenic," contains small quantities of antimony, which may be determined by the method which has just been described.

When, however, antimony and arsenic exist in solution, or when the two metals, being combined in the solid state, are united with other substances besides, so that the method which has just been indicated cannot be employed, another process must be adopted to separate them from each other. The solution is then diluted with a sufficient quantity of water, after having added tartaric acid thereto, without which precaution the addition of water would render it milky. If the combination under examination consists of metals in the reguline state, it is dissolved in aqua regia, tartaric acid is poured in the solution, and water is then added. A current of sulphuretted hydrogen is then passed through the liquor to saturation, it is then very gently heated in order that the metallic sulphurets may settle completely. When the solution contains arsenic acid, it may be easily perceived that the first precipitate formed is one of sulphuret of antimony, and it is only after some time that sulphuret of arsenic falls down, so that at first a layer of an orange-red colour is deposited, which is covered afterwards by another layer of a light yellow colour. It is therefore necessary, before filtering, to intermix these two layers well together by stirring with a glass rod.

The whole is then filtered through a weighed filter, upon which the sulphurets are dried at an extremely gentle heat until their weight remains constant. After having determined the weight of these sulphurets, a portion (about half of it) is shaken down into a glass, the remainder is very gently heated again with the filter, and the whole is weighed, for the purpose of ascertaining the weight of the portion now about to be operated upon. This portion is to be oxydised in the glass, by pouring, with great precaution, aqua regia upon it, in the manner described (page 298) when treating of the oxydisation of sulphuret of antimony. Tartaric acid is then added to the solution, and it is to be diluted

with water. If any sulphur has separated, it must be filtered from the liquor, and its quantity determined. Chloride of barium is now poured in the filtered liquor in order to precipitate the sulphuric acid which has been formed. From the weight of the sulphate of baryta that of the sulphur which it contains is calculated, and that portion of sulphur which has not been oxydised by the aqua regia is added thereto. The whole of the sulphur contained in a given weight of metallic sulphurets having thus been determined, it is easy to deduce therefrom the collective weight of the antimony and arsenic.

Another portion of the metallic sulphurets obtained, is treated in an atmosphere of hydrogen gas, like the sulphuret of antimony in which it is desired to determine the quantity of antimony. The description of this method has been given (page 290). A glass bulb, on each side of which a glass tube is soldered, is weighed, and the suitable quantity of the metallic sulphurets obtained is introduced into it. The glass tubes on each side are then most carefully cleaned with the feather of a pen, and the whole is again weighed, by which means the quantity of the sulphurets under present treatment is ascertained. The apparatus being ready and filled with hydrogen, the bulb is heated, at first gradually and then strongly. The excess of sulphur of the sulphuret of antimony is first disengaged, sulphuret of antimony sublimes next, part of which is converted into metallic arsenic by the action of the hydrogen gas. The operator takes care to expel all the sublimate from the tube with the flame of a small spirit-lamp. It is necessary not to heat strongly the glass bulb for a long time, because some antimony might otherwise sublime with the arsenic, yet the heat must not be too feeble, for otherwise the reduction would not be complete.

When the experiment has been conducted with due care, this method yields satisfactory though not perfectly accurate results. Ordinarily the error does not amount to more than one half per cent.

The quantity of antimony contained in the metallic sulphurets obtained is thus known, that of the sulphur has been

ascertained by a former experiment; the loss indicates that of the arsenic.

This method is preferable to others which have been proposed for separating antimony and arsenic or their oxydes, and which are still less accurate. It is necessary, however, to effect the separation of the sulphuret of arsenic and of antimony in an atmosphere of hydrogen, because by distilling simply in the usual manner, a pretty considerable quantity of sulphuret of antimony volatilises with the sulphuret of arsenic.

It is hardly necessary to caution the operator not to inhale the arsenical fumes, and that the experiment should of course be carried on under the hood of the chimney, and not in the open room of the laboratory.

By this method it may be seen that a very small quantity of antimony in sulphuret of arsenic can be weighed more easily than a very small proportion of arsenic in sulphuret of antimony.

\* Ordinarily, *another method* is resorted to for separating arsenic from antimony. The alloy is first pulverised and then treated by nitric acid until it is completely oxydised; the liquor is then diluted with water, and by filtering, the undissolved oxyde of antimony is separated from the arsenious acid which is in solution. A small quantity of ammonia is also poured in this solution, so as exactly to saturate it, in order to precipitate a small portion of the oxyde of antimony which has dissolved, or else the alloy is treated by aqua regia, the acid solution is evaporated to dryness, in order to evaporate the nitric and muriatic acids, taking care not to heat the mass too strongly, and by adding water the antimonious acid which has formed separates from the arsenic acid; the solution is afterwards exactly saturated with ammonia, in order to precipitate therefrom the small quantity of antimonious acid which might remain in solution.

\* Neither of these two methods, however, yields accurate results, because the oxyde of antimony or antimonious acid obtained generally contains a pretty considerable quantity of arsenious or of arsenic acid, and they cannot therefore be



resorted to for quantitative analysis. They may, however, be employed with advantage for the purpose of examining whether combinations of antimony contain arsenic.

When the alloy is one of arsenic and antimony with other metals, or when the oxydes of arsenic and of antimony are combined with the oxydes of other metals, the combination is dissolved in aqua regia, or, if it be oxydised, in muriatic acid, tartaric acid is added to the solution, and it is diluted with water. The antimony and arsenic are then precipitated by sulphuretted hydrogen, provided that the other metals are not capable of being precipitated from acid solutions by that reagent. The sulphurets of antimony and of arsenic produced are separated by filtering; the filtered liquor is supersaturated with ammonia, and the other metallic oxydes are then precipitated by hydrosulphuret of ammonia, the presence of tartaric acid preventing their being precipitated by other reagents. The metal, the precipitation of which presents most difficulties in that case, is nickel, for it is known that its precipitation by hydrosulphuret of ammonia is attended with great difficulties. When on the contrary the metals combined with antimony and arsenic are capable of being precipitated from acid solutions by sulphuretted hydrogen, their separation should be effected by hydrosulphuret of ammonia.

**DETERMINATION OF ARSENIOS AND ARSENIC ACIDS WHEN THEY  
EXIST SIMULTANEOUSLY.**

When arsenious and arsenic acids are contained simultaneously in an acid liquor, their quantitative separation and determination presents difficulties which have not yet been overcome. It is true that the arsenic might be precipitated by sulphuretted hydrogen, and by analysing the sulphuret thus obtained, the operator might calculate the quantity of the oxygen and of the arsenic contained collectively in the two, and from which he might subsequently calculate how much of these

two bodies belonged to the arsenious and to the arsenic acids ; but it must not be forgotten that the result thus arrived at would be very far from the truth, because the sulphuret of arsenic contains free sulphur from the decomposition of the sulphuretted hydrogen dissolved in the liquor, by which the whole calculation is rendered uncertain.

## CHAPTER XL.

## TELLURIUM.

DETERMINATION OF TELLURIUM, OF TELLUROUS, AND OF  
TELLURIC ACID.

WHEN tellurium exists in a solution in the state of tellurous acid, and has to be determined quantitatively, it is best to reduce it by means of sulphurous acid. The reduced tellurium is collected upon a weighed filter, carefully dried at a gentle heat, and when it no longer loses in weight, it is weighed. The solution of sulphite of ammonia or of soda is preferable to sulphurous acid for this purpose. If the solution of tellurium is alkaline, it is acidified by muriatic acid in sufficient excess to redissolve the oxyde which precipitates at first. The acid liquor is heated in a flask or matras, but not to ebullition, and a small quantity of solution of sulphite of alkali is gradually poured in. The tellurium separates under the form of a voluminous black powder. The operator must take great care that the liquor always contains free sulphurous and muriatic acids; the proportion of the latter should not, however, be too considerable, but it is necessary that enough of it should be present to prevent a precipitation of hydrate of tellurous acid when the solution of the sulphite comes to be added, for in that case the precipitate would remain undecomposed. The more concentrated the liquor is, the more rapid and complete the precipitation is. If sulphite of alkali be added to the cold liquor, the latter at first remains clear and colourless, and it is only after some time

that it begins to turn brown, and that it deposits a black powder, which is tellurium.

\* Some time must elapse before the totality of the tellurous acid can be precipitated in the state of metallic tellurium by sulphurous acid. It is best, according to Berzelius, when the liquor is sufficiently concentrated, to digest it for several days with the sulphurous acid in a warm place and in a corked flask. The metal is then collected on a filter, whilst the liquor exhales the odour of sulphurous acid. The metal must never be left uncovered and exposed to the contact of the air upon the filter for however so short a time before washing it, for in presence of a little muriatic acid it soon oxydises and a little chloride of tellurium is formed, which, dissolving in the filtered liquor which contains free sulphurous acid, renders the latter turbid, because the sulphurous acid reduces the dissolved tellurous acid. It is better, therefore, to pour the clear liquor of the flask upon the filter, and before collecting the tellurium upon the paper it should be washed a little in the flask itself with water containing some sulphurous acid.

\* After the reduction of the tellurous acid by means of sulphurous acid, the operator must never omit to heat again the liquor filtered from the separated metal, or else to ascertain, by a fresh addition of alkaline sulphite, that all the tellurium has been completely separated from the solution, which sometimes is not the case when the operator has not heated for a long time the solution of tellurous acid with the sulphite of alkali.

If the solution of tellurous acid contains nitric acid, the result obtained is uncertain, because free nitric acid may easily redissolve a little reduced tellurium. In order to avoid this difficulty the operator should, before the addition of the sulphite of alkali, gradually pour muriatic acid in the solution, concentrate it by heat, until the muriatic acid added has completely destroyed the nitric acid. It is known that this is done when the solution being exposed to heat exhales the odour of pure muriatic acid without any smell whatever of chlorine gas. The

concentrated solution is then diluted by a little water, and the tellurous acid is afterwards reduced by sulphite of alkali.

\* According to Berthier, nitric acid may also be eliminated from the liquor by evaporating it in the water-bath until the acid be completely destroyed. Should the solution contain muriatic acid, no chloride of tellurium is lost during the evaporation, this substance not being volatile at that temperature.

\* In drying, tellurium shrinks very much, and is reduced after exsiccation to a very small bulk.

\* When a solution contains tellurous acid dissolved in other acids, especially in sulphuric acid, it might be determined by evaporating the liquor to dryness, fusing the dry residuum in a platinum crucible, which volatilises the sulphuric acid, and leaves the tellurous acid in the crystalline state. If tellurium exists in a solution in the state of telluric acid, it (the solution) must be treated by hot muriatic acid, until chlorine gas is no longer disengaged, by which means the telluric acid is converted into tellurous acid, which may then be reduced, as we said, by sulphurous acid.

\* According to Berzelius, when the operator has a solution of tellurates, the telluric acid may be determined as basic tellurate of silver. A slight excess of solution or nitrate of silver is added to the liquor, after which the precipitate is dissolved in ammonia; the liquor is thus evaporated until the excess of ammonia has dissipated, the basic tellurate of silver is collected on a weighed filter, and carefully weighed. The salt contains 79.8 of oxide of silver, and 20.2 of telluric acid. Yet by employing this method, the quantity of telluric acid obtained is always a little less than should be, which, however, does not prevent the determination from being accurate enough to indicate the degree of saturation of the tellurate.

SEPARATION OF TELLUROUS ACID AND TELLURIC ACID FROM  
THE OXYDES OF CHROMIUM, OF URANIUM, OF NICKEL, OF  
COBALT, OF ZINC, OF IRON, AND OF MANGANESE, FROM  
THE EARTHS AND FROM THE ALKALIES.

Tellurous acid is precipitated from its diluted acid solutions by sulphuretted hydrogen in the state of brownish-black sulphuret of tellurium, wherefore this reagent may serve to separate it from the substances which have been first mentioned. The sulphuret of tellurium produced is collected on a filter. If the operator knows it for certain that no other metallic sulphuret has fallen down with it, it might very well be collected on a weighed filter, and after drying it, its weight might be determined, from which the quantity of tellurous acid might be calculated; but the sulphuret of tellurium precipitated often contains an excess of sulphur, which is especially the case when peroxyde of iron is contained in the solution. This precipitated sulphuret must therefore be digested, whilst still moist, in aqua regia, the tellurium is thereby oxydised, whilst the sulphur is partly separated and partly converted into sulphuric acid. The digestion must be continued until the liberated sulphur has acquired a perfectly yellow colour: the solution is then filtered, the nitric acid contained therein is destroyed in the manner described above, and the tellurium is reduced by a solution of sulphite of alkali.

\* When telluric acid is combined with the substances mentioned at the beginning of the preceding paragraph, and has to be separated therefrom, the first operation is to convert it into tellurous acid by treatment with muriatic acid. Telluric acid may also be precipitated by sulphuretted hydrogen; but the transmutation is in that case so slow and so imperfect, that it is best to convert it into tellurous acid.

When metallic tellurium is combined with the metals of oxydes which are not precipitable from acid solution by

sulphuretted hydrogen, the alloy is first dissolved in nitric acid or in aqua regia, and after diluting the solution with water it is treated by sulphuretted hydrogen gas. Strong nitric acid should be employed to dissolve the compound, because if treated by weak nitric acid, a slight disengagement of telluretted hydrogen might sometimes take place.

\* Sulphuretted hydrogen is not the only reagent which can be employed to separate tellurous acid from the metallic oxydes mentioned at the head of the paragraph; the separation is still more easily effected from acid liquors, by means of sulphurous acid, or of sulphite of alkali, because in such solutions, these reagents do not precipitate the oxyde in question. When combinations of metallic tellurium with the metals of these oxydes have been dissolved in nitric acid or in aqua regia, it is sufficient, before precipitating the tellurium, to take care to destroy the nitric acid in the solution as completely as possible. The reduced tellurium sometimes contains small quantities of the metals from which it has been separated by the sulphite of alkali, but this quantity is very trifling.

\* The tellurium is afterwards separated by filtering, and the oxydes contained in the filtering liquor may then be determined by the methods which have been indicated before.

SEPARATION OF TELLUROUS AND TELLURIC ACIDS FROM THE  
OXYDES OF MERCURY, OF SILVER, OF COPPER, OF BISMUTH,  
OF LEAD, AND OF CADMIUM.

Tellurous and telluric acids are separated from these oxydes by hydrosulphuret of ammonia. An excess of this reagent is added to the solution previously saturated by ammonia, and the whole is left to digest for a long time at a gentle heat. The sulphuret of tellurium is thereby dissolved, whilst the sulphurets of the other metals remain insoluble. Although sulphuret of tellurium is very soluble in hydrosulphuret of ammonia, it is advisable to leave the whole to digest for a long time at a very gentle heat.

When metallic tellurium is combined with the metals of the oxydes in question, the combination is dissolved in nitric acid or in aqua regia, the liquor is supersaturated with ammonia and treated as was just said. The sulphuret of tellurium is precipitated from its solution in hydrosulphuret of ammonia by means of very dilute muriatic acid or of acetic acid; this sulphuret is collected on a filter, it is oxydised by treatment with aqua regia, and the tellurium in the liquor is reduced in the manner which has been described above.

\* The same method may be employed for separating tellurous acid from the oxydes of cobalt, of zinc, of iron, and of manganese.

\* The tellurous acid held in solution with some of the oxydes enumerated at the beginning of the paragraph may also be separated therefrom by means of sulphurous acid, or of a sulphite of alkali, when the oxydes are not susceptible of being thus reduced or do not form, as is the case with protoxyde of lead, compounds which are insoluble in the sulphuric acid produced. Oxyde of bismuth and oxyde of cadmium are therefore, among the oxydes named, the only ones from which tellurous acid may thus be separated. This method, however, cannot be adopted even for separating tellurous acid from oxyde of bismuth, because, according to Berthier, an appreciable quantity of bismuth precipitates with the reduced tellurium.

\* Tellurous acid may be separated by means of solution of potash from the oxydes which are insoluble in an excess of this reagent. A great deal of tellurous acid precipitates simultaneously with the oxydes.

\* There is an easy method of separating tellurous acid and oxyde of silver from each other when simultaneously in solution in nitric acid or in another acid. It consists in using muriatic acid, which, when the solution is dilute, precipitates the oxyde



of silver completely in the state of chloride of silver. After having collected the latter upon a filter, the tellurous acid in the filtered liquor is reduced according to the method which has been described before.

\* When a metallic combination of tellurium and silver has to be analysed, it should be dissolved in pure nitric acid. The solution is easily effected with the help of heat. When the solution is complete, it is diluted by water, and the operator should hasten to precipitate the oxyde of silver therefrom in the state of chloride of silver by adding muriatic acid, because if the nitric acid solution was left at rest for some time, crystals of tellurite of silver would be formed.

#### SEPARATION OF METALLIC TELLURIUM FROM OTHER METALS.

When tellurium is combined with other metals in the reguline state it is easily separated from a great number of them by means of chlorine. A given weight of the compound to be analysed is heated in an apparatus similar to that represented (page 212) by passing a current of chlorine over it. Chloride of tellurium distils over, whilst the chlorides of the other metals which are not volatile, remain behind. If the current of chlorine which is passed over the heated telluret is strong, white perchloride of tellurium is produced, but if the current is weak and the heat applied somewhat strong, a black protochloride of tellurium distils over under the form of violet vapours. The chloride of tellurium is led in a flask containing water to which muriatic acid has been added. The perchloride of tellurium dissolves completely in this liquor, whilst, when treated by pure water, tellurous acid separates; protochloride of tellurium, however, dissolves in water mixed with muriatic acid, leaving a residuum of black metallic tellurium. If treated by water alone it would be decomposed, and the result would then be a mixture of tellurous acid and of metallic tellurium.

\* When the operation is at an end, and chloride of tellurium

no longer volatilises, and the whole apparatus has cooled, the tellurous acid dissolved in the liquor of the flask is reduced by sulphurous acid or by a sulphite of alkali. If any metallic tellurium had fallen before in this liquor, it is not necessary to separate it by filtering before reducing the tellurous acid in solution. The metals of the non-volatile chlorides may be analysed afterwards by the methods which have been described before.

This method may be employed for separating tellurium not only from most of the metals hitherto mentioned, but also from gold, with which it is frequently found combined in the native state.

#### SEPARATION OF TELLURIUM FROM ANTIMONY AND TIN.

Antimony frequently accompanies tellurium, from which it can be separated when both metals are contained in solutions, by precipitating the tellurium by a sulphite of alkali. Antimony is not thereby reduced, and may subsequently be precipitated from the liquor filtered from the tellurium obtained.

When the metallic alloys of tellurium are decomposed by chlorine gas, chloride of antimony distils over with the chloride of tellurium. After having dissolved the volatile chlorides in muriatic acid the tellurous acid is separated from the antimonious acid by the means which have just been indicated.

Tin is separated from tellurium in the same manner as antimony.

#### SEPARATION OF TELLURIUM FROM ARSENIC.

Arsenic might be separated from tellurium by the method which is used to separate the latter from antimony.

## CHAPTER XLI.

## SELENIUM.

## DETERMINATION OF SELENIUM AND OF SELENIOUS ACID.

WHEN selenium exists in a solution in the state of selenious acid, the best manner of determining it is by *sulphurous acid* employed as for the determination of tellurium. After having acidified the liquor which contains selenious acid with muriatic acid, a solution of sulphite of alkali is poured into it, the selenium is thereby reduced immediately, in most cases, and separates under the form of a cinnabar red powder which remains for a very long time suspended in the liquor; but by boiling the latter, the reduced selenium shrinks into a very small bulk, and assumes a black colour. If now the addition of a fresh quantity of sulphite of alkali to the solution does not produce a red colour, the reduced selenium is collected on a weighed filter, washed, dried with extreme caution, and when its weight is found to remain constant, its quantity is determined.

It often happens, however, that the reduction of selenium by sulphurous acid is slower. In all cases, it is best, after the metal has separated, to operate exactly in the same manner as was described for the reduction of tellurous acid by sulphurous acid, that is to say, the operator must add to the liquor a fresh quantity of sulphite of alkali, and leave the mixture for a long time at rest in a warm place. If no more selenium precipitates, the operator may conclude that the whole of the selenium had been reduced at first.

When the solution from which the selenious acid has to be determined contains nitric acid at the same time, it is necessary before adding the sulphite of alkali to decompose it completely by muriatic acid. This is done by heating the liquor on a sand-bath, and gradually adding muriatic acid thereto until chlorine is no longer disengaged. The selenium is afterwards precipitated by sulphite of alkali.

#### DETERMINATION OF SELENIC ACID.

When selenium exists in the liquor in the state of selenic acid, it cannot be reduced, according to Mitscherlich, by sulphurous acid. The solution in that case must be boiled with muriatic acid until chlorine is no longer disengaged. The muriatic acid reduces the selenic into selenious acid, which may then be reduced by sulphurous acid, or by a solution of sulphite of alkali gradually added to the acid liquor.

As, however, it is difficult to reduce the last traces of selenic acid into selenious acid by means of muriatic acid, it is best to precipitate the first of these two acids in the state of seleniate of baryta by pouring into it a solution of nitrate of baryta. The seleniate so produced is as insoluble in the dilute acids as sulphate of baryta. It is, therefore, advisable, when the liquor contains a seleniate in solution, to acidify it by a little nitric acid, and then to pour some nitrate of baryta into it. The seleniate of baryta contained is ignited as is done for sulphate of baryta. After ignition it is weighed, and from its weight the quantity of selenic acid is calculated.

\* It is necessary, however, in that case, to be certain that the whole of the selenium in the liquor is in the state of selenic acid, for selenite of baryta is soluble in free nitric acid, and would therefore remain in solution. If the operator has reason to apprehend that the combination under examination contains not only selenic acid but selenious acid also, the compound should be mixed with nitrate of alkali in a porcelain crucible, and the mixture fused for some time, by which means the selenious

is converted into selenic acid. The fused mass is then dissolved in water, the solution is supersaturated with nitric acid, and the selenic acid is precipitated in the state of seleniate of baryta by means of a solution of nitrate of baryta.

\* Selenious acid might also be determined in certain compounds as seleniate of baryta, by fusing the compound with nitrate of alkali, and treating the fused mass as has been just said.

SEPARATION OF SELENIOUS ACID AND SELENIC ACID FROM THE  
OXYDES OF CHROMIUM, OF URANIUM, OF NICKEL, OF COBALT,  
OF ZINC, OF IRON, AND OF MANGANESE, FROM THE EARTHS  
AND FROM THE ALKALIES.

The selenious acid being precipitated from acid solutions by *sulphuretted hydrogen* in the state of yellow sulphuret of selenium, this reagent offers an easy means of separating selenium from the above oxydes, when it exists in a solution in the state of selenious acid. The sulphuret of selenium obtained is removed from the filter whilst still wet, and aqua regia is poured upon it, with which it is left to digest, until the selenium has completely dissolved, and only a slight residuum of sulphur remains. It is best, however, to dissolve it completely by means of fuming nitric acid, because a portion of undissolved sulphur possibly might still retain some selenium. This solution is afterwards digested in muriatic acid until the nitric acid is completely destroyed; after which the solution is diluted with a small quantity of water, and the selenium is precipitated by sulphite of alkali. As, however, the oxydes mentioned at the beginning of this paragraph, are not reduced by sulphurous acid, it is often preferable to begin by precipitating the selenium from the acid liquor, by pouring a solution of sulphite of alkali into it, and after having collected the metal on a filter, the other substances in the filtered liquor are determined.

When the metals of the oxydes in question are combined in

the reguline state with selenium, the compound is dissolved in hot nitric acid or in aqua regia. It is true that by this method the metals are oxydised before the selenium, but by protracting the digestion the latter at last dissolves completely also. Before adding the solution of sulphite of alkali to the liquor, the nitric acid must be destroyed by muriatic acid.

If instead of selenious acid, it is selenic acid which is combined with the alkalies, the earths, or the metallic oxydes in question, the separation of the selenium cannot be effected by sulphurous acid, nor by sulphuretted hydrogen, because these two reagents have no action upon selenic acid. It is necessary in that case to boil the solution with muriatic acid until the selenic acid is converted into selenious acid, or what is better still, a solution of nitrate of baryta is poured in, which immediately precipitates the selenic acid in the state of seleniate of baryta, from the weight of which the quantity of the acid may be determined.

If the combination of selenic acid to be analysed is insoluble in water and in acids, as is the case, for example, with seleniate of baryta, it must be boiled with muriatic acid in order to convert the selenic into selenious acid. The selenites which are insoluble in water, being soluble in acids, the reduction is completed when the combination has dissolved in muriatic acid.

\* The reduction of the selenic acid contained in compounds which are insoluble in acids, into selenious acid, is often, however, very slowly effected by this process. In most cases, therefore, it is best to resort to the following method :—A given weight of the insoluble compound is mixed with four times its weight of carbonate of potash or of soda, and the mixture is then fused in a platinum crucible. The fused mass is then treated by water, which dissolves the seleniate of alkali, and the excess of carbonate employed, and leaves the earths in the state of undissolved carbonates. Nitric acid is then poured in the solution to render it acid, and the selenic acid is precipitated therefrom in the state of seleniate of baryta.

SEPARATION OF SELENIOUS AND SELENIC ACIDS FROM THE  
OXYDES OF MERCURY, OF SILVER, OF COPPER, OF BISMUTH,  
OF LEAD, AND OF CADMIUM.

Selenious acid is separated from these oxydes by means of hydrosulphuret of ammonia. If the compound is insoluble, the operator must endeavour to render it soluble in an acid. The liquor is afterwards supersaturated with ammonia, and hydrosulphuret of ammonia is then poured into it. This reagent dissolves the sulphuret of selenium, whilst the sulphurets of the other metals are precipitated. This method of precipitating selenium from most of the metals which have been enumerated above, is preferable to that by sulphurous acid, because the oxydes of several of these metals are reduced by sulphurous acid.

When a nitric acid solution contains selenious acid, and protoxyde of lead, no other reagent than hydrosulphuret of ammonia can be employed, for if carbonate of ammonia were used to precipitate the protoxyde of lead, the precipitate, even were a large excess of the reagent poured in, would still retain selenious acid. Even when sulphuric acid is resorted to for precipitating the protoxyde of lead from the solution, it is necessary, in order to obtain the whole of the sulphate of lead produced, to evaporate the solution to dryness, and to heat the dry mass until all the free acid, both the selenious and the excess of sulphuric acid, have been completely eliminated. By this method, therefore, the quantity of the selenium cannot be determined.

In the analysis by means of hydrosulphuret of ammonia, the operator proceeds in the same manner as for separating the oxydes of antimony and of arsenic from the metallic oxydes mentioned at the beginning of the paragraph, and a description of which has been given (pages 294—340). Although sulphuret of selenium dissolves easily in hydrosulphuret of ammonia, it is advisable to add an excess of this reagent to the solution

supersaturated with ammonia, and to leave the metals to digest for a long time in a warm place. The metallic sulphurets which have not dissolved are afterwards collected on a filter, they are washed with water to which hydrosulphuret of ammonia has been added, and the quantity of the metals which they contained is then determined by the methods which have been indicated before. The solution in hydrosulphuret of ammonia is acidified with dilute muriatic acid or with acetic acid, by which sulphuret of selenium is precipitated, if the liquor contained selenious acid. The sulphuret of selenium is then collected on a filter, and it is oxydised, whilst still moist, by aqua regia, after which sulphite of alkali is added to the liquor, in order to reduce the selenium, as we said before.

If, on the contrary, mercury has to be separated from selenium by this method, it is necessary to wait until the solution of the sulphuret of selenium has completely cooled before filtering, by which means the sulphuret of mercury produced is separated.

This method may likewise be resorted to for separating manganese, iron, zinc, and cobalt, from selenium.

\* But if the solution contains no selenious acid, but selenic acid combined with the metallic oxydes in question, after having precipitated the latter by hydrosulphuret of ammonia, and separated the metallic sulphurets so produced by filtering, sulphuret of selenium cannot be precipitated by pouring a dilute acid in the liquor, because selenic acid is not convertible into sulphuret of selenium by hydrosulphuret of ammonia. But the solution being acidified, the selenic acid is precipitated by nitrate of baryta in the manner described before, and is determined in the state of seleniate of baryta, wherefore it is unnecessary to separate the bases from selenic acid by hydrosulphuret of ammonia. If the combination of selenic acid with the metallic oxydes in question, which cannot be precipitated from an acid



solution by sulphuretted hydrogen, is soluble in water, it is to be dissolved therein, and the selenic acid is precipitated from the liquor by nitrate of baryta.

\* Sulphuretted hydrogen may be resorted to for precipitating metallic oxydes in the state of metallic sulphurets, since selenic acid is not convertible into sulphuret of selenium by this gas. The selenic acid remains then in solution, and it may be determined in the liquor filtered from the precipitated sulphurets. When, however, this method is adopted, muriatic acid should not be added to the solution, because a little selenic acid might thus be converted into selenious acid, which would produce sulphuret of selenium by treatment with sulphuretted hydrogen.

\* This method is particularly applicable for the analysis of the seleniates which are insoluble in water, and the bases of which are capable of being converted into metallic sulphurets by sulphuretted hydrogen, as is the case, for example, with seleniate of lead. The pulverised compound is first put in a vessel with water, and a current of sulphuretted hydrogen is then passed through it to entire saturation. The sulphuret of lead produced is separated by filtering, and the selenic acid remains in the liquor.

#### SEPARATION OF SELENIUM FROM METALS.

\* The combinations of selenium with metals are dissolved in nitric acid or aqua regia; the metal is thereby converted into oxyde, and the selenium into selenious acid; no selenic acid is produced. The methods which have been previously described are employed afterwards to separate the selenious acid from the metallic oxydes in the solution.

Selenium may also be separated very well from metals by passing a current of chlorine over the compound, and afterwards separating, by distillation, the chloride of selenium formed, and which is volatile, from the other metallic chlorides which are fixed. The metallic seleniurets are much more easily and

rapidly decomposed by chlorine than the metallic antimoniurets or arseniurets: wherefore this method is much to be recommended for the analysis of metallic seleniurets. The apparatus used for the purpose is similar to that represented (page 212). It is advisable that the diameter of the glass tube soldered to the bulb *e* and bent at right angle be not too small. A given weight of the seleniuret is introduced into the glass bulb *e*, the apparatus is then mounted. When quite filled with chlorine gas, the bulb is then heated with the smallest flame which can be produced with an argand spirit lamp, and as soon as the chloride of selenium is formed it immediately volatilises. At first an oily liquid of an orange-yellow colour appears, it is protochloride of selenium, and it runs by the tube into the flask *k*, one-third full of water, and in which this chloride undergoes a decomposition, the result being to liberate selenium, which, however, is redissolved for the most part by the current of chlorine which passes through the liquor, yet a slight portion of selenium often remains at the bottom of the vessel under the form of globules. Afterwards perchloride of selenium only is produced, which condenses in the tube bent at right angle, and which, if too small, it might obstruct: wherefore it is necessary to heat this tube by the flame of a small spirit-lamp, in order to drive into the flask the perchloride which deposits in the tube.

\* Most metallic seleniurets are so easily decomposed by chlorine gas, that half an hour after filling the apparatus with chlorine, all the selenium is completely converted into chloride, when operating upon a few grammes of the compound. The experiment is at an end when, after having driven as much as possible, by the flame of a small spirit lamp, the perchloride of selenium from the bulb, no fresh quantity of it is formed. The bulb is then allowed to cool gradually, the portion of the tube is cut with a good file, and the perchloride of selenium which it may contain is pushed out, or made to fall into the flask, which must then be closed immediately.

The metallic chlorides in the bulb are afterwards analysed by the methods which have been described before. When lead

alone is combined with selenium, it is well to begin by weighing the glass bulb with the metallic chloride, and then to weigh the bulb alone, by which means the weight of the chloride of lead is ascertained. But in presence of copper, it is useless to determine the weight of the metallic chlorides. If the compound contains iron, a portion of perchloride of iron is found with the non-volatile chlorides, whilst the other volatilises with the perchloride of selenium.

The liquor of the flask *k* is heated until the free chlorine has volatilised; muriatic acid is then added to it, and the selenium is precipitated by means of a sulphite of alkali. But, though it is easy to precipitate the selenium completely from a solution of selenious acid, by means of sulphurous acid, yet the precipitation is difficult when a current of chlorine gas has been passed for a long time through an aqueous solution of perchloride of selenium. The solution of selenious acid assumes a cinnabar red tinge shortly after the addition of sulphurous acid, but it often occurs that the latter does not at first produce any precipitate whatever, which proves that selenic acid must have formed. A long ebullition with muriatic acid is required to enable the sulphite of alkali to precipitate the selenium completely. The liquor filtered from the reduced selenium must be kept for a long time, boiled a second time with muriatic acid, and sulphite of alkali should be again added to it in order to see whether the whole of the selenium has been reduced. If the seleniuret contained iron, the quantity of this metal which during the analysis has distilled with the perchloride of selenium, is determined in the liquor filtered from the selenium.

\* This method is advantageous when the seleniuret contains *lead*, only it is necessary in that case to heat the combination with much care whilst treated by chlorine, otherwise a little chloride of lead might volatilise with the chloride of selenium.

\* If the seleniuret contains mercury, which is often the case, the *mercury* is by this method converted into protochloride of

mercury (*corrosive sublimate*), which volatilises with the perchloride of selenium, and dissolves in the liquid of the flask *k*, and it may be separated from the selenium as described before.

\* *Another method* may also be employed to analyse compounds of selenium with a great number of metals. After having pulverised the seleniuret, it is fused with a mixture of carbonate and of nitrate of alkali, until completely oxydised. The fused mass is treated by water, which dissolves seleniate, nitrate and carbonate of alkali; this solution is then supersaturated with nitric acid, and selenic acid is precipitated therefrom in the state of seleniate of baryta, by means of nitrate of baryta. The oxydised metal remains behind, when insoluble in carbonate of alkali, which is generally the case. It is then washed, dissolved in muriatic acid, and its quantity is then determined by the methods which have been described before.

#### SEPARATION OF SELENIUM FROM TIN, ANTIMONY, AND ARSENIC.

\* The oxydes of these metals contained in solutions with selenious acid may be separated from it by reducing the latter by means of sulphurous acid, which has no reducing action upon them. If they have to be separated from selenic acid, it is to be converted into selenious acid, by means of muriatic acid, and then reduced by means of sulphurous acid. After having separated the reduced selenium, the metallic oxydes are precipitated from the filtered liquor by the methods which have been described before.

\* Selenic acid may also be separated from arsenic acid in solutions, by adding thereto a solution of nitrate of baryta and some free nitric acid, which dissolves the arseniate of baryta, but not the seleniate of that base. The latter is collected upon a filter and weighed, from which the weight of the selenic acid is calculated.

\* If a solution contained selenic acid simultaneously with the

*oxydes of antimony, of tin, and arsenious acid*, the operator should endeavour to dissolve them in muriatic acid, and, after diluting the acid liquor with water, to precipitate the selenic acid in the state of seleniate of baryta; if any of the oxydes of antimony are present, tartaric acid must be added to the liquor before diluting it. Heat must be altogether avoided, because this might reduce a portion of the selenic into selenious acid.

\* The seleniurets of arsenic may be fused with a mixture of nitrate and of carbonate of alkali, until they be completely oxydised. The fused mass is dissolved in water, nitric acid, and a solution of nitrate of baryta are added to the liquor, and the seleniate of baryta which precipitates is separated.

\* If, however, the seleniuret of arsenic contained a considerable quantity of other metals, it would be difficult to avoid all loss by fusing it with carbonate and nitrate of alkali; even by using a large proportion of carbonate. Wherefore in rigorous analytical researches it is best to oxydise the compound completely, or nearly so, by nitric acid or aqua regia, cautiously to add an excess of carbonate of soda to the solution, if it contained still a sufficient quantity of free nitric acid, to evaporate the whole to dryness, and to fuse the residuum. The fused mass is then treated as just said.

#### SEPARATION OF SELENIUM FROM TELLURIUM.

When, in the course of an analysis, these two substances have been precipitated simultaneously by sulphurous acid, they are fused with a mixture of carbonate and of nitrate of alkali at a temperature which should not be too high; nitric acid and nitrate of baryta are added to the solution of the fused mass, and the undissolved seleniate of baryta is separated by filtering from the tellurate of baryta in solution. Telluric acid is reduced into tellurous acid in the filtered liquor by means of muriatic acid, and then the tellurous acid is afterwards reduced by means of sulphurous acid.

\* A loss may, however, take place during the fusion of the

selenium and tellurium with the carbonate and nitrate of alkali : wherefore it is better to treat the selenium containing tellurium by nitric acid or by aqua regia, and then, when it has been oxydised for the most part, and a considerable portion of nitric acid still exists, an excess of carbonate of soda is added, the whole is evaporated to dryness, and the dry residuum is fused. The fused mass is then treated as has just been said.

When selenious acid has to be separated from tellurous acid, the solution containing them should be evaporated to dryness, and the residuum is treated by a mixture of carbonate and of nitrate of alkali, as we have said. The solid compounds containing selenious acid are treated in the same manner.

DETERMINATION OF SELENIOUS AND OF SELENIC ACID WHEN  
THEY EXIST SIMULTANEOUSLY.

The quantities of selenious and of selenic acid when they exist together in a solution is easily determined. The selenic acid is first determined in the state of seleniate of baryta in the liquor acidified with nitric acid, and the quantity of the selenious acid is afterwards ascertained by means of sulphuretted hydrogen or of sulphurous acid.

## CHAPTER XLII.

## SULPHUR.

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DETERMINATION OF SULPHUR.

THE quantitative determination of sulphur may be effected with great precision. The sulphur is converted into sulphuric acid, which is then precipitated by a salt of barium, and from the weight of the sulphate of baryta obtained the quantity of the sulphur is calculated. The *modus operandi* consists in digesting the combination of sulphur in nitric acid or in aqua regia, by which means it is oxydised and dissolved in the acid. The sulphur is always converted by the excess of acid employed into sulphuric acid, and never into a less degree of oxydisation. A large quantity of acid and a prolonged digestion are necessary, however, to transform the sulphur completely into sulphuric acid. In most cases the metal combined with the sulphur is oxydised long before that body; ordinarily the oxyde produced is dissolved *in toto*, whilst as yet the greatest portion of the sulphur is entire; the sulphur is found after a long digestion, with the help of heat, into agglomerated yellow lumps, or, after a shorter digestion in the form of a yellow powder at the bottom of the vessel. As the complete oxydisation of the sulphur would require too long a time, the solution is diluted with water, and when the sulphur has separated therefrom with its characteristic yellow colour, it is collected upon an accurately-weighed filter, well washed, dried at a temperature as low as possible until the

weight remains constant.<sup>1</sup> The sulphuric acid produced is separated from the above filtered liquor by pouring a solution of chloride of barium into it, and, from the weight of the sulphate of baryta produced, that of the sulphur which it contains is calculated. The sum of the two quantities of sulphur indicate collectively the weight of that substance contained in the compound submitted to analysis.

When *fuming nitric acid* is employed to oxydise a substance which contains sulphur, the action is much more violent than when a weaker acid or aqua regia are employed. When a sulphur-compound, being previously pulverised, is afterwards treated by a sufficient excess of fuming nitric acid, ordinarily there is no separation of sulphur, and the whole of it is converted into sulphuric acid. Fuming nitric acid, however, is not always used, because its employ requires great caution. In order, in such case, to avoid the loss of a small quantity of the compound by projection, it is best to put it in a matrass, and to pour the fuming acid upon it by small portions at a time, by means of a funnel, taking care to add a fresh portion only after the violent reaction which it produces each time has abated. A large quantity of water is then added to the oxydised mass, and if all the sulphur has dissolved, the sulphuric acid formed is precipitated by a solution of chloride of barium.

\* *Another and safer method* of proceeding for oxydising the sulphur compound to be analysed, consists in pulverising the substance and weighing it in a small glass-tube of a sufficiently large diameter, and closed at one end; it is then introduced into

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<sup>1</sup> Certain metallic sulphurets may advantageously be treated by a mixture of muriatic acid and of chlorate of potash, which rapidly converts the sulphur into sulphuric acid. According to M. Karsten, iron pyrites reduced into fine powder and boiled with a solution of chlorate of potash, without addition of muriatic acid, are rapidly decomposed, the whole of the sulphur being converted into sulphuric acid, and the iron into peroxyde of iron.

Mr. Millon, however, prefers a mixture of nitric acid and of chlorate of potash, which, with the help of heat, reacts violently; pure sulphur may thus be rapidly converted into sulphuric acid.—Ed.



a flask containing a suitable quantity of fuming nitric acid, and this flask is closed immediately with a well-fitted glass stopper. The flask must be pretty capacious, otherwise the violent action of the acid upon the compound might break it or force the stopper out. When the reaction has ceased, the stopper is removed from the flask, and heat is applied to the latter.

The sulphate of baryta obtained in these operations is more difficult to wash than is generally the case, because, in presence of nitric acid, and of an excess of the barytic reagent, some nitrate of baryta is precipitated along with the sulphate, which cannot be separated from it except by a protracted washing with hot water.

\* It often happens, during the washing of this sulphate of baryta, that after the acid liquor has percolated clear through the filter, the water used for washing passes milky through it, wherefore the filtering-paper used should not be too fine. This milkiness, however, can be obviated as follows:—The sulphate of baryta having completely settled at the bottom of the acid liquor, the clear supernatant liquor is first poured on the filter to within about one-eighth of an inch from the precipitate. A large quantity of boiling water is then poured over this precipitate, the whole is well stirred, and left to digest for a long time in a warm place. The supernatant liquor is then poured out upon the filter to within a short distance from the precipitate, and a fresh quantity of boiling water is poured upon the precipitate as before. This treatment is repeated once or twice, and the milky mixture of sulphate of baryta and water is finally thrown upon the filter. It is necessary, however, to take care, after filtering the clear liquor, to receive the water used for washing in another vessel, in order, if it passes milky, not to have too large a quantity of liquid to filter. The water used for washing, when turbid, cannot be clarified except by repeated filterings. The small quantities of sulphate of baryta suspended in it require a long time to settle.

The other operations of the analysis of the ordinary compounds

of sulphur is very simple. The operator has only to determine the other oxydes dissolved by nitric acid or aqua regia, which exist in the filtered liquor. But as the excess of baryta which has been employed to precipitate the sulphuric acid might be a source of error, it is best to begin by separating it from the liquor, which is done by adding sulphuric acid to the latter, taking care, however, not to use a great excess of it. The sulphate of baryta produced is collected on a filter, and after washing it, it may be thrown away. This sulphate is very easily washed, because, since there is an excess of sulphuric acid, it can contain no nitrate of baryta. This being done, the oxydes contained in the compound are then precipitated.

SEPARATION OF SULPHUR FROM COPPER, CADMIUM, NICKEL,  
COBALT, ZINC, IRON, AND MANGANESE.

Most of the combinations of sulphur with the metals can be analysed by the method which has just been described; those of sulphur, with copper, cadmium, nickel, cobalt and zinc can be so treated, but there are, however, several compounds, especially those of sulphur and manganese, and also a few of those of sulphur and iron, for which pretty strong and hot nitric acid, or strong and hot aqua regia must be employed. If a very weak and cold acid were used, a slight disengagement of sulphuretted hydrogen might very well take place, which would of course produce a loss of sulphur. It is best also to operate upon these compounds in the pulverised state, and not in lumps, because the latter become oxydised only at the surface, and become thus covered with a coating of sulphur, which often protects them from the action of the acid.

The sulphur which is separated in these analyses has ordinarily a grey colour at first, but should never be collected upon a filter before it has become of a pure yellow, which takes place by prolonging the digestion. It is then completely dried upon a weighed filter, its weight is determined, and it is afterwards burnt, in order to ascertain whether it was perfectly pure. This is done as follows:—As much of it as possible is removed from

the filter, and heated in a small counterpoised platinum crucible, by which means it is volatilised. If a fixed residuum is left, it ordinarily consists of the oxyde of the metal with which the sulphur was combined.

\* Sometimes, however, when operating upon native sulphurets, this residuum is quartz, or some other species of rock.

The oxyde was naturally contained in the state of metallic sulphuret in the liberated sulphur, but was converted into basic sulphate by being heated in contact with the air; which basic sulphate being almost always in very small quantity, generally loses all its sulphuric acid under the influence of a very high temperature. From the weight of the remaining oxyde, the quantity of the metal which it contains is calculated; and, by deducting it from that of the sulphur, the true quantity of this latter substance in the compound is ascertained. The operator then dissolves the oxyde in muriatic acid, which generally leaves a small portion of matrix and of silica, as residua; this is separated by filtering, and the weight thereof is determined. This is often the case with the native sulphurets, but it also frequently happens with the artificial sulphurets. The solution of the small quantity of oxyde is mixed with a solution of a barytic salt, in order to see whether the ignited residuum should not perchance have retained some sulphuric acid. If a precipitate of sulphate of baryta is thus produced, the quantity of sulphuric acid which it contains is determined, and deducted from that of the oxyde which has been found; the small portion of sulphur remaining in the said oxyde is next determined, and added to the quantity of the sulphur previously obtained. I, however, must repeat that when the quantity of the oxydes is small, and they have been exposed to a strong red heat, they retain no sulphuric acid. If the quantity of the remaining oxyde is more considerable, that is, if above one or two centigrammes, the operator may rest assured that the sulphur which was weighed was not of a pure yellow colour.

\* When, during the oxydisation of the metallic sulphuret by nitric acid or aqua regia, the sulphur has separated under the

form of a cohesive mass of a yellow colour, from which the acid liquor can be decanted, it is very advantageous to do so, and thus to avoid filtering through a weighed filter, for the weighing of a filter and of a substance of whatever kind along with it is always attended with troublesome contingencies. The sulphur is washed with a large quantity of hot water, dried in the vessel which holds it, but at a temperature which should not be capable of melting it; it is then weighed in a small porcelain capsula until the weight remains constant, and it is burnt in that capsula.

\* Instead of the method which has just been described the following may be resorted to for the analysis, not only of the sulphurets under present consideration, but of nearly all other sulphurets. A certain portion of the compound is to be reduced into fine powder, and mixed with three times its weight of pulverised nitrate of potash or of soda, to which about as much carbonate of soda is to be added. The fusion is best effected in a porcelain crucible, upon an argand spirit-lamp. The fused mass is treated by water.<sup>1</sup> The fusion with the nitrate of alkali converts the whole of the sulphur into sulphuric acid. The water added dissolves the sulphate thus produced and also the nitrate, nitrite, and carbonate of alkali, and leaves the metals in the state of oxydes. They are then washed and dissolved in muriatic acid, they are then separated and their quantity is determined by means of the methods which have been described before. The solution is saturated with muriatic acid, and the sulphuric acid is precipitated therefrom by chloride of barium.<sup>2</sup>

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<sup>1</sup> It is better to employ hot than cold water for the purpose, or rather the fused mass should be boiled with water. Before doing this, however, the mass should have been kept in a state of fusion for some time, in order to insure complete decomposition, and the mass must be allowed to become cold before treating it by water.—Ed.

<sup>2</sup> Dr. Kemp proposed the following method of analysing metallic sulphurets, but more especially sulphuret of copper: The sulphuret is first reduced into very fine powder, and mixed in a glazed porcelain crucible by means of a spatula or smooth glass rod, with about three times its weight of chlorate of potash, and placed in a test tube of strong Bohemian glass. The portions which adhere to the glass rod are wiped away with some chlorate of potash, and the mortar in which the mixture has been

\* The only metallic sulphurets which cannot very well be treated in this manner are those which contain a large excess of sulphur, and which lose a portion of it by heat alone. With such sulphurets the reaction which takes place whilst fusing is too violent, so that a loss may thus take place. And, moreover, when the compound contains some *gangue*<sup>1</sup> the above mentioned process is not very suitable.

\* Some other combinations of sulphur require a somewhat different method of analysis.

#### SEPARATION OF SULPHUR FROM LEAD.

The combination of sulphur and of lead is first pulverised, and then converted into sulphate of lead, by fuming nitric acid. This salt is subsequently treated as described page 162. When, however, the operator wishes to know accurately the quantity of sulphur contained in such a compound, it is best to treat it by chlorine gas, in the manner which will be described farther on. This method is more especially applicable when the sulphuret of lead is combined with other metallic sulphurets. In which case the usual method of analysis is attended with some difficulty.

\* In effect, when such a compound is treated by aqua regia, the sulphur which separates may contain not only some sulphate, but chloride of lead also, wherefore nitric acid must be employed instead of aqua regia. When the sulphur has not been completely oxydised by the treatment with that acid, which can be the case only if fuming nitric acid has been employed, it is a proof that that which has separated contains sulphate of lead. The precipitate should then be collected on a weighed filter, unless the acid liquor can be decanted from the sediment as

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performed is likewise rinsed with some chlorate of potash, which is added to the mixture in the tube, which is then to be exposed to good red heat from top, to bottom; by which means the mass becomes immediately oxydised. This being done, the contents of the tube, when cold, are washed out with hot water, treated with muriatic acid, filtered, washed, and the silica, sulphuric acid, and metallic oxyde is determined as usual.—Ed.

<sup>1</sup> *Gangue* (Bergart) is the name of the rock to which a metallic ore is adhering.—Ed.

above said. The sediment being washed and weighed it is ignited in order to burn the sulphur, the weight of which is determined from the difference in the weighings. The remaining sulphate of lead is weighed, and from its weight all the quantity of the oxyde of lead which it contains, and also that of the sulphuric acid, or, rather, that of the sulphur and of the lead, is calculated.

\* The liquor filtered from the sulphate of lead and sulphur contains no sulphuric acid, or only very slight traces, because the sulphuric acid produced by the oxydisation of the sulphur has formed sulphate of lead, a very small proportion of which only can have dissolved. Wherefore, a very small quantity only of solution of nitrate of baryta, or of chloride of barium must be added; if chloride of barium is used, an excess of it must be carefully avoided, because it might precipitate a little chloride of lead, which is very sparingly soluble. From the very small quantity of sulphate of baryta produced, that of the sulphur which it contains is calculated. Dilute sulphuric acid must not be resorted to for the purpose of eliminating the excess of baryta employed, for this acid would, of course, precipitate sulphate of lead. The best is to employ sulphuretted hydrogen, which will precipitate, in the state of sulphurets, the oxyde of lead in solution and the other metals contained in the liquor; these sulphurets are subsequently examined by the methods which have been described before.

\* In most cases the analysis of the compounds of sulphur may be abbreviated by treatment with nitrate and carbonate of alkali, as we have said.

#### SEPARATION OF SULPHUR FROM BISMUTH.

The combination of sulphur and of bismuth must be decomposed by pure nitric acid alone, and not by aqua regia. The liberated sulphur must be washed with water to which a little nitric acid has been added, until all the oxyde of bismuth has been removed. Carbonate of ammonia is then poured in the filtered liquor in

order to precipitate the oxyde of bismuth, and after having filtered the solution, and carefully acidified it by muriatic acid, the sulphuric acid is precipitated therefrom by solution of chloride of barium.

#### SEPARATION OF SULPHUR FROM SILVER.

The combinations of sulphur with silver must also be decomposed by pure nitric acid, the sulphur liberated is separated from the liquor, and the oxyde of silver is precipitated therefrom by muriatic acid. The liquor is again filtered to separate the chloride of silver produced, and the sulphuric acid contained in the filtrate is precipitated by chloride of barium. We should observe, that the liberated sulphur must be very well washed with hot water, because the sulphate of silver produced is a salt which is very sparingly soluble in water. In order to render it more soluble, a few drops of nitric acid may be added to the water used for washing.

In this analysis, it is necessary to guard most carefully against the nitric acid solution of the sulphuret of silver, or of the substance which contains it, absorbing the slightest trace of muriatic acid, from any fumes which may be disengaged in the laboratory, because the liberated sulphur might thus be contaminated by chloride of silver.

#### SEPARATION OF SULPHUR FROM MERCURY.

The combinations of sulphur with mercury must be treated by aqua regia, for nitric acid alone has no action upon them; the whole of the sulphur is thus often oxydised. The sulphuric acid is first precipitated by chloride of barium, and afterwards the quantity of mercury is determined. This operation, however, presents difficulties, on account of the presence of nitric acid. The best is to precipitate the mercury by a current of sulphuretted hydrogen, which method has already been spoken of, page 202.

## SEPARATION OF SULPHUR FROM GOLD AND PLATINUM.

Sulphur is eliminated from these compounds by igniting them, the metals remain in the pure state, and their quantity is determined; that of the sulphur is indicated by the loss.

## SEPARATION OF SULPHUR FROM TIN.

The combinations of sulphur with tin may be oxydised by aqua regia; yet it is better to decompose them by chlorine gas, according to the process which will be described farther on.

## SEPARATION OF SULPHUR FROM TITANIUM.

The combination of sulphur with titanium is strongly ignited in the air, in order to convert the titanium into titanic acid, from the weight of which, the composition of this substance, if quite pure, may be determined. When, however, the operator wishes to know immediately the quantity of sulphur which the compound contains, it is better to oxydise it by fuming nitric acid so as to convert the whole of the sulphur into sulphuric acid, water is subsequently added, and the titanic acid is precipitated by ammonia, which is to be separated by filtering; the liquor is then acidified by muriatic acid, and the sulphuric acid is precipitated by chloride of barium. The compound may also be decomposed by chlorine gas, according to the method which will be described presently.

## SEPARATION OF SULPHUR FROM ANTIMONY AND ARSENIC.

The combinations of sulphur with antimony, arsenic, and other metals, may be analysed by the methods which have been described before in the chapters treating of the metals in question.



## SEPARATION OF SULPHUR FROM TELLURIUM.

\* When the combination has been decomposed by *aqua regia*, the sulphur must be left for a long time in contact with this acid, in order to free it entirely from tellurium. The sulphuric acid is then separated in the usual way, the tellurous acid is reduced by sulphite of alkali, after having previously filtered the liquor from the sulphate of baryta produced, and separated the excess of the baryta employed.

## SEPARATION OF SULPHUR FROM SELENIUM.

\* This separation is effected in the same manner as that of sulphur from tellurium. If the combination has been converted into selenic and sulphuric acids by fusion with nitrate of alkali, these acids are separated by means of a method, which will be described farther on.

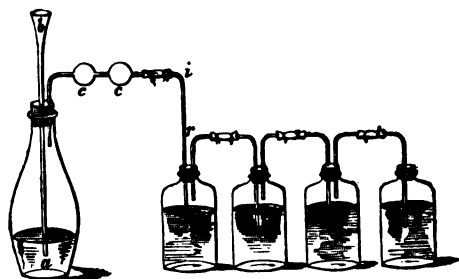
SEPARATION OF SULPHUR FROM THE METALS OF THE ALKALIES  
AND EARTHS.

The combinations of sulphur with the metals of the alkalies, and alkaline earths, are difficult to analyse, because sulphuretted hydrogen is always disengaged, even when they are treated by the most oxydising acids. Fuming nitric acid cannot always oxydise them without loss, for even this acid often disengages traces of sulphuretted hydrogen from the compound. The best way of dissolving such combinations without loss, consists in weighing the sulphuret of alkali in a small glass, and in treating them by fuming nitric acid in a large flask, which is closed as rapidly as possible with a well adjusted glass-stopper, as was said, page 377.

When such combinations are contained in solutions, they may be analysed by decomposing them by an acid; the oxyde of the alkaline metal thus produced combines with the acid employed, and its quantity may then be determined by the methods which

have been described before. The quantity of the sulphur is known from the loss. If the operator wishes to determine it in a direct manner, it is customary to determine the bulk of the sulphuretted hydrogen which is disengaged pending the decomposition by means of an acid. It is better, however, to combine the sulphur with a metal, and to determine the quantity of this substance contained in the metallic sulphuret produced.

The method employed to effect this, in some particular cases, is the following:—The weighed solution of the metallic sulphuret, or the dry compound of sulphur and of alkaline or earthy metal, is put in a bottle *a*, which, like all the other bottles of the apparatus, must be of moderate size. The bottle *a*, is closed with a tight cork, perforated with two holes to admit the stem of a funnel *b*, which reaches nearly to the bottom of the bottle, and a disengagement tube, which is connected with another tube *i*, by a small tube of Indian rubber; this tube *i*, passes through the cork of another bottle *d*, and plunges about



an inch into the liquid which it contains. This cork is also perforated with a second hole which admits another tube *r*. The two-thirds of bottle *d*, are filled with a metallic solution, and the tube *r*, opens about half an inch above the surface of the liquid, and is bent at right angle, as represented in the figure. Four other bottles *d, e, f, g*, are connected in the same manner; all the corks fit the bottles quite tight, except the last, which is loose. For the metallic solution to be put in the bottles, a solution of acetate of lead may be chosen. From the weight of the sulphuret of lead obtained, and which is weighed after

having dried it, the quantity of the sulphuretted hydrogen which has been decomposed is calculated. Yet it is better to fill the bottles with a solution of chloride of copper.<sup>1</sup> Wherefore the three first bottles *d, e, f*, are to be filled, as was said, with a neutral solution of this salt, but the solution of the same salt in the fourth bottle *g*, is rendered alkaline by ammonia, because such a solution absorbs sulphuretted hydrogen much better and much more rapidly than a simple solution of chloride of copper.

If instead of a solution of the metallic sulphuret, the operator have employed such a sulphuret in the solid form, the bottle *a*, must be filled with boiled distilled water, and the stem of the funnel *b*, must plunge much below the surface; the operator then pours very cautiously through the funnel the acid by which he intends to decompose the sulphuret, taking care to pour only small portions of it at a time. Dilute nitric or muriatic acids are ordinarily preferred for the purpose. This produces a disengagement of sulphuretted hydrogen, which is absorbed by the solutions contained in the bottles, the result being a production of sulphuret of copper which precipitates. The operator must manage the experiment so that the disengagement goes on very slowly, because if the current were too rapid, a small portion might perchance escape absorption. This slow disengagement may be managed by adding the acid with care. It is necessary that the glass tubes should not plunge too deeply in the metallic solution.

When the disengagement of the sulphuretted hydrogen has completely ceased, the empty space of bottle *a*, is still filled with it, and the acid solution retains also a small portion of this gas. In order that as little sulphuretted hydrogen as possible should remain dissolved in the liquor, a small quantity of water only should be added to the metallic sulphuret before decomposing it. But

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<sup>1</sup> A solution of acetate of lead is not so good, because the sulphuretted hydrogen gas disengaged is mixed with some muriatic acid, owing to which the precipitated sulphuret of lead is contaminated by chloride of lead, which cannot be eliminated by washing without great trouble.—Ed.

that the sulphuretted hydrogen gas may be completely expelled from bottle *a*, it is absolutely requisite, after the disengagement has completely ceased, and the solution in the bottle has become very acid, to heat it with care and for a long time, and when it has cooled completely, to pour gradually into it a concentrated solution of carbonate of ammonia; a disengagement of carbonic acid is thereby produced, which drives all the sulphuretted hydrogen into the other flasks, where it is absorbed.

The absorption being at an end, the apparatus is then taken asunder, and the sulphuret of copper produced is collected on a filter as rapidly as possible. It is not necessary to wash it, but it must be oxydised, and the sulphuric acid formed is afterwards precipitated by a barytic salt. From the sulphate of baryta thus obtained, the quantity of the sulphur in the compound under examination is determined. In order to oxydise completely all the sulphur and sulphuret of copper, it is best to employ fuming nitric acid. If, however, the operator wishes to avoid using this acid, and to employ ordinary nitric acid or aqua regia, the sulphuret of copper must be oxydised without the filter, in order to be able to determine the sulphur which separates, but this is by no means easily done.

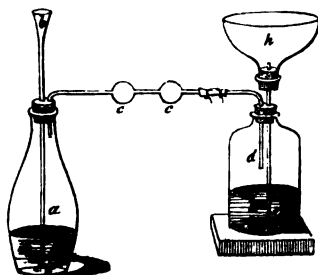
*Sulphate of copper*, which is cheaper, must not be substituted for that of solution of *chloride of copper*. Should it be used, however, the sulphuret of copper obtained should be well washed, but during the washing a portion is liable to become oxydised, which happens especially when the solution has previously been rendered ammoniacal.

When a solution of *acetate of lead* has been employed, it must not be rendered ammoniacal if the operator intends to weigh the sulphuret of lead formed, in order to determine, from its weight, the quantity of sulphur contained in the substance.

This method of determining sulphur in a substance by converting it into sulphuretted hydrogen is especially to be recommended when, besides sulphuretted hydrogen, other gases, such as carbonic acid or hydrogen, are disengaging during the treatment, which gases are not capable of being absorbed by

the metallic solution, at least that contained in the three first bottles *d*, *c*, and *f*.

When the operator is certain that nothing but sulphuretted hydrogen is disengaged during the decomposition, a less complicated apparatus may be employed. The bottle *a*, in which the disengagement is effected is the same as in the preceding apparatus. The cork which closes it admits likewise a funnel *b*, with a very long neck descending nearly to the bottom ; it is also provided with a disengagement tube connected with another glass tube *d*, by one of caoutchouc. This glass tube *d*, is bent at right angle as before, and goes through a cork which closes hermetically a flask *e*, half filled with a metallic solution ; the tube *d*, does not plunge in the liquid, and terminates at about an inch



from the surface. The cork admits besides a second straight tube *e*, which descends nearly to the bottom of the bottle. The other end of the tube above the cork passes through a flask *h*, from which the bottom has been removed. A large medicine phial [or Florence flask] from which the bottom has been cut off answers the purpose very well. This flask is connected with the tube *e*, by means of a cork through which the latter passes, and protrudes a little way up. All the joints must be perfectly tight.

This apparatus being erected, dilute sulphuric or muriatic acid is cautiously poured through the funnel into the bottle ; this produces a disengagement of sulphuretted hydrogen which passes into the flask *e*, and causes the metallic solution to ascend

into the flask *h*. The pressure produced promotes the easy absorption of the sulphuretted hydrogen in the bottle *e*. As soon as no more gas is disengaged, the acid liquor of bottle *a*, is gradually heated, and after cooling, a little solution of carbonate of ammonia is carefully poured in through the funnel, in order to produce a disengagement of carbonic acid, which completely expels the sulphuretted hydrogen from the flask.

The metallic solution, which is used in preference to put in the bottle *e*, is that of chloride of copper with an excess of ammonia, which absorbs also the carbonic acid which is subsequently disengaged. When the whole of the sulphuretted hydrogen has been absorbed, and the liquor has descended from the flask *h* into the bottle *e*, the apparatus is disconnected with care, and the metallic sulphuret produced is collected and treated as above said.

In these operations, in which a metallic sulphuret has been decomposed, the quantity of oxyde which has been dissolved by the acid poured in bottle *a* must also be determined. Pure sulphur may also have separated in this bottle during the decomposition, which is always the case when the degree of sulphuration of the metallic sulphuret analysed is higher than the degree of oxydisation of the metal. In that case the operator must take care that the liquor contained in bottle *a*, remains acid even after the addition of carbonate of ammonia. The liberated sulphur is collected on a weighed filter, dried, and weighed, after which the quantity of the oxyde is determined. This is ordinarily done in the following manner:—the solution is evaporated to dryness, and the dry residuum is ignited. After having expelled the ammoniacal salt, the remainder is the oxyde combined with the acid employed, or, when muriatic acid has been employed, the residuum consists of the metal of that oxyde combined with chlorine.

If, however, the operator can dispose of a tolerably large quantity of the sulphuret to be analysed, it is advisable to weigh another portion of it, and to decompose it by an acid solely for

the purpose of determining the quantity of oxyde produced. When this is done it is not necessary, as in the preceding analysis, instituted for the determination of the sulphuretted hydrogen, to employ carbonate of ammonia for the purpose of disengaging carbonic acid: carbonate of potash may be used for the same purpose.

When the metallic sulphuret to be analysed is difficult to weigh, a portion of it is to be decomposed without weighing; the relative proportion of oxyde and of sulphur produced indicate the composition of the substance.

\* The most ordinary and easy method of determining the quantity of sulphur in a soluble sulphuret of alkali is the following:—The solution is introduced into a glass stoppered flask with an excess of solution of chloride of copper or of solution of lead. When the sulphuret of copper or of lead has completely deposited, it is collected on a filter, and from its quantity that of the sulphur is determined in the manner which has been described before. After having passed a current of sulphuretted hydrogen in the liquor filtered from the metallic sulphuret in order to decompose the excess of chloride of copper or of solution of lead which it contains, the operator may, by filtering the liquor again, determine the metal of the alkali which it contains, in the state either of chloride or of oxyde.

#### SEPARATION OF SULPHUR FROM SEVERAL METALS IN COMPOUND SULPHURETS.

The combinations of sulphur with most metals may also be analysed in the following manner:—A given weight of the substance is treated in an apparatus similar to that represented page 112. After passing a current of chlorine gas over it, chloride of sulphur distils over, whilst most of the metals remain combined with the chlorine. The chloride of sulphur formed is received, as we have said in speaking of the treatment of the volatile chlorides, into a bottle, one fourth of the capacity of which is filled with water.

In this experiment the operator must take care that the current of chlorine gas is not too rapid. The chloride of sulphur, being decomposed by the water in which it is received, resolves itself into sulphur and sulphurous acid, which is completely converted into sulphuric acid when the empty part of the flask is filled with moist chlorine gas;<sup>1</sup> wherefore, the combination under examination must not be heated before the whole apparatus, including the empty part of the flask which serves as a receiver, is full of chlorine, which is very readily known by the peculiar colour of the gas; and the heat applied must not be more elevated than that which can be produced with the smallest flame of an argand spirit-lamp. The heat must especially be very gentle when the compound under examination contains lead, for the chloride of lead might be volatilised by a strong heat with the other volatile chlorides. The sulphur, liberated by the decomposition of the chloride of sulphur, separates under the form of drops which remain liquid for a long time.

Besides chloride of sulphur, the volatile metallic chlorides distil over, the non-volatile metallic chlorides remain in the bulb. By means of the flame of a small spirit-lamp the volatile metallic chlorides and the chloride of sulphur are constantly driven towards the flask, where they are dissolved and decomposed by the water contained therein. The operation is at an end when volatile chlorides cease to come from the glass bulb *a*, from which the heat is gradually removed, and when quite cold the apparatus is disconnected. It is necessary to take care before disconnecting the apparatus to expel the volatile metallic chlorides, in such a way that the glass tube be free from them as far as *h*, (page 212). This tube is then cut off at *h*, by means of

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<sup>1</sup> It is generally admitted that the chlorides of sulphur in coming in contact with water, are decomposed, forming muriatic acid, and hyposulphurous acid, the latter undergoing a further decomposition into sulphurous acid, and sulphuric acid, sulphur being at the same time deposited. But it appears from the recent experiments of MM. Fordos and Gélis, that hyposulphurous acid is never met with amongst the products of the decomposition of chloride of sulphur by water, and that the sulphur, sulphuric and sulphurous acids are secondary products resulting from an alteration of the thionic acids, which are at first formed.—Ed.



a fine file, and the lower part so cut is allowed to fall into the flask *k*, which is then to be immediately closed with a well-ground glass stopper, for the metallic chlorides contained in this lower portion of the tube are suddenly decomposed by the water of the flask *k*, owing to which, when a large quantity of chloride of sulphur is at once decomposed, such a disengagement of heat is produced, that a certain portion of these substances might escape in vapour before the water could have time to act upon them. If a small quantity of volatile metallic chlorides still remain in that part of the glass tube which is not cut off, that part is likewise to be separated and washed with water, which is afterwards added to that of the flask *k*. This being done, the weight of the non-volatile metallic chlorides may be determined, by weighing the glass bulb with its contents, and weighing it again after having emptied and dried it. As this bulb had been weighed with the glass tube soldered on each side before the substance to be analysed had been introduced into it, it is sufficient, after having cleared and dried the parts of the tube which were cut, to weigh them with the glass bulb and its contents, by which means the weight of the non-volatile metallic chlorides is determined. If the compound contained copper it is useless to weigh the non-volatile metallic chlorides, because they consist of a mixture of subchloride and protochloride of mercury.

\* The analysis of the non volatile metallic chlorides is performed by the methods which have been fully described before. They are first treated by muriatic acid and water in contact with the air. If the compound contains copper, the subchloride of copper produced dissolves completely after some time, because under the influence of the muriatic acid and of the oxygen of the air, it is converted into protochloride of copper. If it contains silver at the same time, this metal remains undissolved in the state of chloride of silver: and if, besides silver, it contains lead also, water is sufficient to separate completely the chloride of lead from the chloride of silver. The chloride of lead dissolved is afterwards separated from the protochloride of copper by sulphuric acid, as we said, page 184. If the non-volatile

metallic chlorides contained chloride of iron and chloride of zinc, they can be separated by sulphuretted hydrogen from the lead and copper in the solution, but of course the chloride of silver must previously be removed.

The liquid in the receiver holds the volatile metallic chlorides in solution, when soluble therein ; this liquid contains also sulphuric acid and sulphur, the quantity of which must first be determined. When, after the complete decomposition of the substance under examination, the operator continues to pass chlorine gas in the liquid of the receiver, he may sometimes succeed in dissolving completely the sulphur which at first precipitated, and in converting it into sulphuric acid ; but several days are often required to produce this effect ; the operator, however, needs not entertain any fear about the success of the experiment during that time, provided the disengagement of the gas is, as usual, very slow.

When the decomposition is finished, the receiver is exposed to an extremely gentle heat, until all the free chlorine is expelled. If the liquid contains sulphur in a free state, the operator waits a little before collecting it on a filter, not only because it remains liquid for a long time, but because, after having warmed the liquor, it remains viscid for some time. When it has become quite hard it is collected on a weighed filter, dried and weighed.<sup>1</sup> A solution of chloride of barium or some other barytic salt is poured in the filtered liquor in order to precipitate the sulphuric acid produced, and from the quantity of sulphate of baryta thus formed, that of the sulphur which it contains is calculated. The quantity of the oxydes, the metals of which have distilled over in the state of chlorides along with the chloride of sulphur, are determined in the liquid filtered from the sulphate of baryta.

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<sup>1</sup> The sulphur remains thus liquid or viscid for several hours, and the liquor containing it must be left at rest until it (the sulphur) has completely solidified. Of course, it must be washed as well as dried before weighing it, and the water used for washing is added to the filtered liquor, in which the sulphuric acid has to be determined by chloride of barium.—Ed.

When the combination submitted to analysis contains sulphuret of antimony, and, if the operator wishes to decompose it by chlorine gas, the liquid put in the bottle which serves as a receiver, must consist of a weak solution of tartaric acid, to which muriatic acid has been added. After the decomposition, the operator begins also by separating the liberated sulphur; after which, the sulphuric acid is separated by means of a salt of baryta, and the antimony is subsequently precipitated by means of a current of sulphuretted hydrogen. Yet it is necessary, before precipitating the antimony, to remove the excess of the salt of baryta employed by means of sulphuric acid, a great excess of which, however, must be avoided. I should observe again, that the sulphate of baryta, the quantity of which is to be determined, must be collected on a filter as soon as it has completely deposited, because, if the liquor is left several days without filtering, crystals of acid tartrate of baryta, are formed therein, notwithstanding the presence of muriatic acid, which it is difficult to remove from the sulphate of baryta by washing.

\* In rigorously accurate analysis, it is advisable to treat the ignited sulphate of baryta by muriatic acid, as we have said, page 289.

If, besides sulphuret of antimony, the substance submitted to analysis contains also sulphuret of arsenic, it is likewise necessary to put a solution of tartaric acid in the bottle which serves as a receiver. This precaution, however, is not necessary, when sulphuret of arsenic alone is present. In the first case, both the arsenic and antimony are precipitated together in the state of metallic sulphuret, by means of sulphuretted hydrogen, and the sulphuret of arsenic is separated from that of antimony, in the manner described, page 348.

When the metallic sulphurets, which the operator wishes to decompose by chlorine gas, contain sulphuret of iron, a certain quantity of perchloride of iron is volatilised, it is true, but the

whole of the iron cannot be thus expelled with the other volatile metallic chlorides, and with the chloride of sulphur, because too high a temperature must not be employed to decompose the metallic sulphurets. On the other hand, it is impossible to manage the experiment, in such a manner that all the perchloride of iron shall remain with the non-volatile metallic chlorides; wherefore, in such a case, chlorine gas is passed over the heated substance, until no other volatile metallic chlorides, except perchloride of iron, are volatilised; the latter is easily recognised by the yellowish-brown colour of its gas, and the crystalline spangles which it produces when it is shifted along the tube where it is deposited, by means of a small spirit-lamp; this distinguishes it very well from the other more volatile chlorides. As soon as no more perchloride of iron volatilises, the heat is removed, and the apparatus is allowed to cool. The greater part of the perchloride of iron is found in the glass-bulb with the non-volatile metallic chlorides, from which it may be separated in the manner indicated before; the much less considerable portion of this perchloride of iron which has distilled over with the volatile metallic chlorides, is separated afterwards.

If the substance submitted to analysis contained antimony, and the operator has, on this account, been obliged to dissolve tartaric acid in the liquid of the bottle which serves as a receiver, the antimony is first precipitated by sulphuretted hydrogen, and the sulphuret of antimony is collected on a filter; the filtered liquor is supersaturated with ammonia; and hydrosulphuret of ammonia is then added thereto in order to precipitate the iron, for, in such a case, this latter substance cannot be determined in any other way, on account of the presence of tartaric acid. The sulphuret of iron thus obtained is converted into peroxyde of iron by the method which has been described, page 86.

When the sulphuret which is decomposed by chlorine gas

contains sulphuret of zinc, and provided too strong a heat has not been employed during the decomposition, the chloride of zinc produced remains altogether with the non-volatile metallic chlorides. But if too strong a heat has been employed, the volatile chlorides are accompanied by a very small quantity of chloride of zinc, which may be separated by the methods described before. If the substance under examination contains antimony, the zinc is precipitated in the state of sulphuret, along with the sulphuret of iron; the two metallic sulphurets are then oxydised, and the oxydes may then be separated from each other.

The use of chlorine gas for the decomposition of metallic sulphurets, is a method much to be recommended, especially when the substance to be analysed contains a great number of metallic sulphurets. It is the only one which can be employed for the analysis of compounds which contain simultaneously sulphuret of antimony and sulphurets the metals of which form with chlorine combinations which are insoluble or sparingly soluble in water and in acids, as, for example, sulphuret of silver and sulphuret of lead, which are frequently found in nature combined with sulphuret of antimony. The metals of these sulphurets may, it is true, be separated from each other by means of hydrosulphuret of ammonia, but it may be readily seen, that it would be impossible afterwards to determine the quantity of the sulphur. When the operator wishes to oxydise these metals by aqua regia, the insoluble chloride of silver and sparingly soluble chloride of lead are mingled with the liberated sulphur; if treated by nitric acid, oxyde of antimony or antimonious acid is obtained, mingled with sulphur. The sulphur might be completely oxydised by fuming nitric acid, but as nitric acid does not entirely separate oxyde of antimony, a small portion of which always remains in solution, the method which consists in decomposing these metallic sulphurets by chlorine gas is preferable to all others.

All metallic sulphurets are decomposed by chlorine gas, but

they are not all decomposed with the same facility. The combinations of sulphuret of antimony and of sulphuret of arsenic with the basic metallic sulphurets, which form part of the compounds to which Berzelius has given the name of sulphur-salts, are those which are most easily and completely and rapidly decomposed. Chlorine gas is especially applicable to the decompositions of these substances, especially when the sulphuret of antimony or that of arsenic is combined with metallic sulphurets the metals of which are capable of being precipitated from acid solutions, which is almost always the case.

If, however, the sulphuret of antimony or that of arsenic is combined with sulphurets of iron or of other metals which cannot be precipitated from acid solutions by sulphuretted hydrogen, it is better to oxydise by aqua regia than by chlorine gas. The metallic sulphurets are then dissolved in aqua regia, and, if sulphuret of antimony is present, tartaric acid is added to the liquor, which must besides be suitably diluted with water. The liberated sulphur is then separated by filtering, and the sulphuric acid which has formed is precipitated by a barytic salt. Sulphuric acid is then added to the filtered liquor, in order to eliminate the excess of the barytic salt employed, and, by means of sulphuretted hydrogen, the antimony and arsenic are subsequently precipitated. The liquor filtered from the sulphuret of antimony and of arsenic is then supersaturated with ammonia, and the iron or the other metals which cannot be precipitated from acid solutions by sulphuretted hydrogen are then precipitated by means of hydrosulphuret of ammonia. The presence of tartaric acid does not permit the use of any other reagent to effect this. The only circumstance in which chlorine gas is to be preferred to aqua regia for such a compound, is when it contains nickel, because this metal is precipitated with difficulty from neutral or ammoniacal solutions by hydrosulphuret of ammonia.

The length of time required for the decomposition of metallic sulphurets by chlorine varies. The combinations of sulphuret of antimony and of arsenic with basic metallic sulphurets, such as

grey copper,<sup>1</sup> sulphuret of silver and antimony, bournonite,<sup>2</sup> all are completely decomposed, if operating upon a few grammes, in the course of one hour after the apparatus has been filled with chlorine, and heat has been applied. In effect, chlorine gas decomposes them for the most part, even in the cold, when passed over them for a long time, so that the subsequent application of heat is then of no other use than to separate the volatile metallic chlorides produced from those which are not volatile; the latter will be found to contain no portion of the substance. Simple metallic sulphurets are not so easily decomposed, and the combinations of metallic sulphurets with arseniurets and antimoniuurets, such as bright white cobalt [sulpho-arsenide of cobalt] and nickel glanz [sulpho-antimonial nickel], are less rapidly decomposed. When the experiment is carried on a few grammes of these substances, they may be heated for twelve hours or more, passing a current of chlorine gas over them, and yet not suffer complete decomposition.

\* After having passed gaseous chlorine for a long time in the cold over a sulphuret, it is necessary to use great caution in beginning to heat the bulb of the apparatus, in order that the liquor of the bottle should not ascend into the bulb, which would break it. It often happens, after having begun to heat it, that the as yet undecomposed portion of the compound absorbs enough gaseous chlorine to create absorption of the liquor in the bottle. If, in order to prevent this absorption, too large a proportion be at once poured in the flask, the current of

<sup>1</sup> This variety of grey copper containing antimony and arsenic, dissolves in nitric acid, but a precipitate of antimony is produced, and emits an odour of arsenic when heated before the blow-pipe.—Ed.

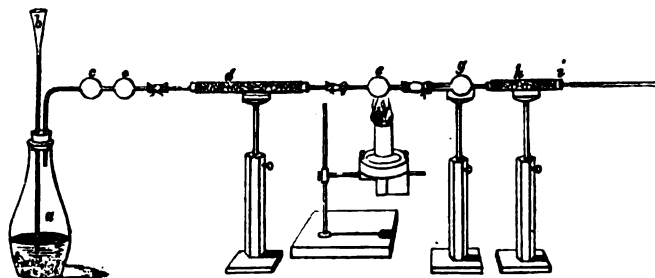
<sup>2</sup> Bournonite is a combination of sulphuret of lead, sulphuret of copper, and sulphuret of antimony. A sample analysed by H. Rose, was found to have the following composition :—

Lead . . . . .	40.84
Sulphur . . . . .	20.31
Antimony . . . . .	26.20
Copper . . . . .	12.65

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100.00—Ed.

being converted into a reguline metal, by being heated in an atmosphere of hydrogen gas ; but of all the metallic sulphurets which combine with metallic oxydes, that of antimony is the only one which behaves in this manner. The combinations of sulphuret of antimony with oxyde of antimony may be decomposed by hydrogen gas in the following apparatus, which is the same as that described, (page 103).



The sulphuretted hydrogen gas produced during the experiment is disengaged, whilst the water formed at the expense of the oxygen of the oxyde is partly condensed in the glass bulb *g*, and partly absorbed by the chloride of calcium in the tube *h*. The quantity of the metal reduced, and that of the water produced, are determined, from which that of the oxyde is easily calculated, and from the latter, that of the metallic sulphuret. If the compound contains only a small quantity of oxyde, or, if only a small portion of the compound is submitted to analysis, the glass bulb *g* may be dispensed with, and the tube of the bulb *e* may be immediately connected with the tube *h*.

This method of analysis is preferable to another, which consists in trying to separate the oxyde from the sulphuret of antimony, by means of a weak acid, or of an acid salt, such as supertartrate of potash, for example ; for, when the combination so treated is in a state of extreme division, a certain quantity of sulphuret of antimony is liable to be decomposed by protracted boiling with water, and cream of tartar.



If the compound to be analysed consists of metallic sulphurets and oxydes which cannot be reduced by hydrogen gas, they must be submitted to the treatment ordinarily employed in the analysis of metallic sulphurets alone. A certain quantity is weighed and digested with nitric acid or aqua regia, and the quantity of sulphur and that of the sulphuric acid produced are determined ; that of the metallic oxyde is subsequently ascertained, part of which existed originally in that state, whilst another portion is the result of the action of the nitric acid employed. It is easy afterwards to calculate the quantity of the sulphuret and of the oxyde.

#### DETERMINATION OF SULPHURIC ACID IN SULPHATES.

The manner in which sulphates are to be analysed may be partially anticipated from that which has been said before on the same subject. The sulphates which are soluble in water are dissolved in this menstruum, and the sulphuric acid is precipitated by the solution of a baryta-salt, for which purpose chloride of barium in most cases is preferred. If sulphuric acid has to be precipitated from the neutral solution of a sulphate, by means of the solution of a salt of baryta, it is advisable previously to acidify the liquor by means of a little muriatic acid. When this liquor contains free ammonia, it is necessary to supersaturate it with muriatic acid, because after having added the solution of baryta-salt, the precipitate formed would consist not only of sulphate, but also, after some time, of carbonate of baryta.

From the weight of the sulphate of baryta obtained, the quantity of the sulphuric acid which it contains is calculated. Before submitting the filtered liquor to further examination, it is customary to separate the excess of baryta employed, by means of sulphuric acid, after which the quantity of the base which was combined with the sulphuric acid is determined.

But if the sulphate to be analysed is insoluble in water, which is the case of several basic sulphates, it is dissolved in muriatic acid or in nitric acid ; the solution is then diluted by water and mixed with a solution of baryta-salt.

When the sulphates are insoluble also, or at least sparingly soluble in acids, another process must be adopted. The combinations which sulphuric acid forms with baryta, strontia, lime, and oxyde of lead are in this predicament. Sulphate of lime is completely decomposed when, after having been reduced to powder, it is boiled with an excess of a solution of carbonate of potash or of carbonate of soda. The result is an insoluble carbonate of lime; it is collected on a filter, washed, dried, and its weight is determined. It may also be ignited after weighing, but as it might lose a little carbonic acid by ignition, it should then be treated, as is the case for oxalate of lime which has been ignited, by a solution of carbonate of ammonia, in the manner and with the precautions mentioned (page 24). The liquor filtered from the carbonate of lime contains, besides sulphate of alkali, the excess of carbonate of alkali employed. It is acidified by cautiously pouring muriatic acid into it, and afterwards solution of chloride of barium is added, which produces a precipitate of sulphate of baryta from the weight of which the quantity of the sulphuric acid is calculated.

The other insoluble, or sparingly soluble sulphates, cannot be completely decomposed, except by fusion with carbonate of potash, or of soda. A portion of the insoluble sulphate reduced into very fine powder, is mixed in a platinum crucible with three parts of alkaline carbonate, and the whole is heated to fusion. If sulphate of lead is present, the operator must avoid too strong a heat, and to continue it too long, which might cause the reduction of a small quantity of lead, which would spoil the crucible. In such a case, the heat should not be urged so as to produce complete fusion.

The ignited mass is afterwards softened with water. If the combination contains no oxyde of lead, but baryta and strontia only, the residuum left by the water consists of carbonate of baryta, and of strontia, which, after being washed, are to be dissolved in muriatic acid. The quantity of each earth in the solution is afterwards determined by the methods which have been indicated before. The liquor filtered from the earthy

carbonates contains sulphate of alkali, and the excess of alkaline carbonate employed; it is then cautiously supersaturated by muriatic acid, and a solution of chloride of barium is poured into it, in order to precipitate the sulphuric acid. From the weight of the sulphate of baryta obtained, the quantity of sulphuric acid which this salt contains, and which existed in the combination submitted to analysis, is calculated.

When the sulphate contains oxyde of lead, the water by which it is treated, after ignition with carbonate of alkali, leaves a trace of this oxyde. If the operator does not intend to determine the quantity of sulphuric acid, the oxyde of lead may be immediately precipitated from the solution in the state of sulphuret of lead, by means of hydrosulphuret of ammonia; but if the quantity of sulphuric acid in the liquor has likewise to be determined, the latter must be supersaturated by nitric acid, and the sulphuric acid is precipitated by means of a solution of nitrate of baryta. The sulphate of baryta produced is separated by filtering; a little solution of sulphuretted hydrogen is added to precipitate the traces of lead in the state of sulphuret. That which has remained undissolved, when the mass which was fused with alkaline carbonate was treated by water, consists of oxyde of lead. This residuum is ignited, if the oxyde is pure, in a porcelain crucible, and its quantity is determined; or if it contains other substances, such as peroxyde of iron, for example, it is dissolved in nitric acid, and it is separated from such foreign substances by the methods which have been described before.

\* SEPARATION OF SULPHATES FROM METALLIC SULPHURETS.

Considering that several metallic sulphurets, such as those of potassium and of sodium, which are soluble in water, are soluble in alcohol also, whilst most sulphates are, on the contrary, insoluble in this menstruum, sulphurets and sulphates may thus, in a very great number of cases, be separated from each other when the combination to be analysed is in the solid state. This is the case with the combinations of sulphates of alkalies with

their corresponding sulphurets, which compounds are always produced when alkaline carbonates are heated with sulphur. The combination is digested in alcohol, in a glass stoppered flask, and the sulphate insoluble in that menstruum is washed with it; it is then dried, ignited, and its weight is determined.

\* If the compound contained any undecomposed alkaline carbonate besides, this salt, being insoluble in alcohol, remains with the sulphate. The quantity of sulphur in the alcoholic solution of the metallic sulphuret might be determined by adding thereto an excess of an alcoholic solution of a metallic salt, the metal of which might form an insoluble sulphuret; for example, an alcoholic solution of chloride of copper. The solution of the metallic sulphuret must be contained in a glass stoppered flask, and the precipitation must be effected in this flask, in order to avoid as much as possible the contact of the air. After having separated the sulphuret of copper which will have formed, it is completely oxydised, without washing it, by fuming nitric acid, and the quantity of the sulphur is calculated from that of the sulphuric acid produced, and which is subsequently precipitated by solution of chloride of barium. Instead of the quantity of the sulphur, that of the metal in the solution of the metallic sulphuret might be determined.

\* The separation of sulphuret of barium, and of sulphate of baryta, when existing simultaneously in a compound, may be obtained by means of hot water only, freed from atmospheric air, and out of the contact of the air.

\* If the combination of the sulphuret with the metallic sulphate can be analysed only in the state of aqueous solution, a portion of the liquor is devoted to the determination of the quantity of the metallic sulphuret which it holds in solution, by means of the solution of protochloride of copper; that of the sulphuric acid is determined in another portion of the liquor, and from the latter, the quantity of the sulphate is calculated. The best manner of performing this experiment consists in pouring in the solution some chloride of barium, which precipitates

the sulphuric acid in the state of sulphate of baryta. But, as in some cases the liquor may contain carbonate of alkali, the precipitate of sulphate of baryta may then be contaminated by carbonate of baryta. It is therefore always advisable to decant the supernatant liquid from the precipitated sulphate of baryta, and to treat the latter by muriatic acid. If the sulphate of baryta should contain any precipitated sulphur, it is of no consequence, because by igniting the salt, the sulphur will volatilise.

#### SEPARATION OF SULPHURIC ACID FROM SELENIOUS ACID.

\* When these two acids exist simultaneously in a solution, the operator may, after having added muriatic acid, separate them from each other by means of solution of chloride of barium, which precipitates the sulphuric acid in the state of sulphate of baryta, because the selenite of baryta formed at the same time remains dissolved in the free muriatic acid. The sulphate is collected on a filter, and the selenious acid is precipitated afterwards, in the state of selenium, by means of a sulphite of alkali.

\* The same method is employed to separate these two acids and their salts.

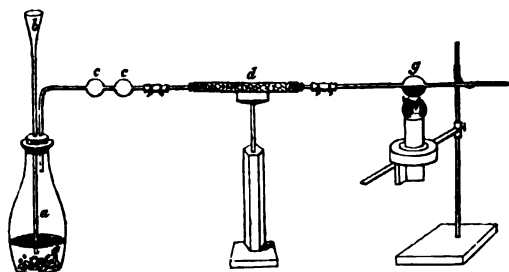
#### SEPARATION OF SULPHURIC ACID FROM SELENIC ACID.

When these two acids exist together, either in the free state, or in the state of salts, their solution must be concentrated, or if the salts are in the dry state, they must be dissolved in a small quantity of water; muriatic acid is added, and the whole is boiled until all odour of chlorine has ceased, and all the selenic acid is converted into selenious acid, which may then be separated from sulphuric acid in the manner indicated above.

The separation of those salts which are insoluble in water and in acids is performed in the same manner by ebullition with muriatic acid. Considering, however, that in such a case the reduction of the selenic acid into oxyde of selenium is very difficult to effect by means of muriatic acid, the following

method, proposed by Berzelius, may be resorted to, at least for the separation of the sulphate and selenite of baryta.

\* A weighed quantity of the substance is introduced in



the above apparatus, which has been described (page 128), in which it is heated in an atmosphere of hydrogen gas. The seleniate of baryta is thereby reduced into seleniuret of barium, with so much violence that a disengagement of light sometimes takes place, but the sulphate of baryta remains untouched. The appearance of the mass remains the same. When water ceases to be formed, the mass is treated by dilute muriatic acid, which dissolves the seleniuret of barium under disengagement of seleniuretted hydrogen. This experiment should be performed under the hood of the chimney, because seleniuretted hydrogen is a gas which has a violent action on the membrane of the nose. The sulphate of baryta remains undissolved; ordinarily, the atmospheric air contained in the muriatic acid decomposing a little seleniuretted hydrogen communicates a light red colour to the liquor; the sulphate may, however, be easily freed from this colour by digesting it in aqua regia, or, which is more simple still, by igniting it.

#### SEPARATION OF SULPHURIC ACID FROM ARSENIOS AND FROM ARSENIC ACIDS.

\* When these acids exist in the free state, or under the form of salts, muriatic acid is added to their solution, and a solution of baryta-salt is next added. If the salts be insoluble in water,

they are to be dissolved by muriatic acid, or in certain cases by nitric acid, and a solution of a baryta-salt is then poured in the acid liquor, previously diluted with water. Sulphuric acid alone is precipitated thereby in the state of sulphate of baryta; the arseniate and arsenite of baryta remain dissolved in the free acid. The quantities of these acids are afterwards determined by precipitating them in the state of sulphuret of arsenic by means of sulphuretted hydrogen. The operator, however, must previously remove the excess of baryta by means of dilute sulphuric acid, which precaution must also be taken when these acids are determined by Berthier's method, (page 337).

SEPARATION OF SULPHURIC ACID FROM VANADIC ACID AND  
OXYDE OF VANADIUM.

\* Sulphuric acid may be separated from vanadic acid simply by the action of heat, but if the quantity of sulphuric acid has to be determined in a solution containing vanadic acid and deutoxyde of vanadium, it may be done by means of a solution of chloride of barium, but, according to Berzelius, when, before precipitating it, the liquor has been acidified by muriatic acid, the sulphate of baryta thus obtained retains still, after having been washed, a little vanadic acid, owing to which it has, when moist, a bluish, and after ignition a yellowish tinge. This sulphate is weighed and fused with sulphate of potash, which then becomes yellow. The fused mass is treated by water, and after having well washed the sulphate of baryta, it is ignited and weighed. The loss indicates the small quantity of vanadic acid which has precipitated with it in the first instance. The liquor filtered from the sulphate of baryta is treated in the cold by sulphuric acid in order to precipitate the baryta; it is evaporated to dryness; the residuum is ignited in order to remove the sulphuric acid, and the vanadic acid is obtained. That small portion of vanadic acid which had precipitated with the sulphate of baryta must be taken account of, and added to the above residuum of vanadic acid.

## SEPARATION OF SULPHURIC ACID FROM CHROMIC ACID.

The best way of separating sulphuric acid from chromic acid, and the sulphates from the chromates, consists in treating the combination like that of sulphuric and of selenic acids, and to proceed as follows:—The combination is dissolved in a little water, and, after having added a sufficient quantity of muriatic acid, the liquor is carefully boiled until the odour of chlorine has disappeared, after which it is diluted with water. The oxyde of chromium which has formed must first be precipitated by ammonia. The liquor is filtered, acidified by muriatic acid, and the sulphuric acid is precipitated in the state of sulphate of baryta by means of a solution of a baryta-salt. The operator may also proceed inversely, that is to say, precipitate first the sulphuric acid by means of a salt of baryta, and then the oxyde of chromium by ammonia; in the latter case, however, the operator must take care, before effecting the second precipitation, to remove the excess of baryta in the liquor by means of sulphuric acid, otherwise the precipitated oxyde of chromium would be contaminated by it, (page 328).

Alcohol must not be added to the muriatic acid in order to hasten the reduction of the chromic acid into oxyde of chromium, because in that case the whole of the sulphuric acid would not be precipitated in the state of sulphate of baryta.

\* It is by ebullition also with muriatic acid that these two acids are separated in such of their combinations as are insoluble in water and in acids. Yet it is necessary to reduce these combinations into very fine powder, or even to levigate them, for otherwise the sulphate which remains undissolved might retain a certain quantity of undecomposed chromate which would impart a colour to it. The insoluble compound might also be fused with carbonate of alkali, and the two acids are then determined by the method employed for the insoluble sulphates and seleniates (page 404).



## DETERMINATION OF SULPHUROUS ACID IN SULPHITES.

\* In order to determine sulphurous acid in the state of gas, peroxyde of lead may be employed, sulphurous acid absorbing this oxyde completely, and being thereby converted into sulphuric acid, which forms sulphate of lead. The quantity of the sulphurous acid gas is determined from the volume absorbed. The peroxyde of lead may be put in a small glass covered with a piece of kid glove, after which the glass is introduced into the sulphurous acid gas, by passing it through the mercurial trough by means of a steel piano-wire. If the peroxyde of lead has been previously weighed, the increase of weight may furnish the means of determining the quantity of the sulphurous acid.

\* Sulphurous acid gas being absorbed by borax, this substance may serve to separate it from other gases, and especially from carbonic acid. Gay Lussac's method for separating sulphuretted hydrogen from carbonic acid, (which method will be described farther on), may also be successfully employed for separating sulphurous acid gas and carbonic acid gas from each other.

\* The best method of analysing the combinations of sulphurous acid with the bases, consists in oxydising them and converting them into sulphates, which are then treated in the manner mentioned before. Care must, however, be taken in oxydising these combinations. When the solution is a concentrated one, it is necessary to add strong nitric acid or aqua regia thereto, and to digest the whole for a long time, with the help of heat, in order to oxydisise the sulphurous acid completely. In order to prevent all disengagement of sulphurous acid, it is advisable to heat the solution before adding the strong nitric acid. It is better, however, to use fuming nitric acid.

\* But if the solution of the sulphites is dilute, or if sulphurous acid exists in a free state in the liquor, it cannot be well

oxydised by nitric acid. It is preferable then, to pass a current of chlorine gas through the solution until the conversion into sulphuric acid be complete. The operator must not neglect to heat the liquor, and to continue the stream of chlorine gas through it for some time. A solution of baryta-salt is then added to the liquor, and from the quantity of sulphate of baryta obtained that of the sulphurous acid is calculated.

When the sulphites which are to be analysed are in the dry state, they are put in a glass-stoppered flask and oxydised therein by strong nitric acid, as has been described before, when treating of the oxydisation of sulphurets (page 376). The sulphite being oxydised, if the base be not volatile, and if the salt be a neutral salt, the oxydised mass may be ignited in a platinum crucible. The residuum is a neutral sulphate.

The solid sulphites are more readily oxydised by fusion with nitrate of potash than by treatment with fuming nitric acid. A certain quantity of the salt to be analysed is to be weighed, pulverised, and mixed with four or five times its weight of nitrate of potash in powder, and a small quantity of nitre is further laid upon the mixture. The whole is gradually heated in a porcelain crucible until it begins to fuse, the sulphurous acid is thereby transformed into sulphuric acid under disengagement of nitrous acid. If the nitrate of potash has been mixed with its own weight of carbonate of potash or of soda, the mixture may be heated in a platinum crucible over the spirit-lamp. Water is poured upon the mass after it has cooled, by which it is dissolved, provided it contains none of the bases which form insoluble compounds with sulphuric acid. The solution is afterwards supersaturated with muriatic acid, the sulphuric acid is precipitated by a solution of chloride of barium, and from the quantity of sulphate thus obtained, that of the sulphurous acid is calculated.

\* Instead of nitrate of potash, the chlorate of that base may

be employed, but it is advisable to mix it with carbonate of potash or of soda, and to mix this mixture with the sulphate which it is intended to analyse. The mixture is exposed to a cherry-red heat in a platinum crucible, after which the ignited mass is treated like that which has been fused with nitre.

#### DETERMINATION OF HYPOSULPHURIC ACID AND OF ITS SALTS.

\* If hyposulphuric acid or its salts exist in concentrated solutions, strong nitric acid is employed to oxydise them, as is done for the sulphites. Heat must be applied, because it is impossible to oxydise them in the cold. The solution may also be oxydised by passing a stream of chlorine gas whilst the liquor is kept warm. The sulphuric acid produced by the oxydisation of the hyposulphuric acid, is precipitated by a solution of a salt of baryta, and from the sulphate thus precipitated, that of the hyposulphuric acid is calculated.

\* When neutral hyposulphates in the dry state are analysed by means of fuming nitric acid, the mass must not be evaporated to dryness, nor the dry residuum ignited, because the oxydisation produces acid sulphates, neutral sulphates, and an excess of sulphuric acid. The mass which has been oxydised by nitric acid, must, therefore, be diluted with water, and by adding a solution of baryta-salt, the operator determines the quantity of sulphuric acid thus obtained.

\* The oxydisation or conversion of the combinations of hyposulphuric acid into sulphuric acid, may be effected like that of the sulphites by fusing the hyposulphates in a platinum crucible with nitrate or chlorate of potash, mixed with carbonate of potash or of soda. The ignited mass is afterwards treated like that which results from the sulphites which have been oxydised by the same means. Yet the oxydisation of hyposulphates requires more care than that of sulphites, because the reaction is a little more energetic.

The dry hyposulphates may also be analysed by igniting a known weight thereof. After ignition there remains a neutral sulphate, the quantity of which is determined, sulphurous acid and water of crystallisation being disengaged during the treatment. The sulphuric acid in the sulphate contains half more sulphur than the hyposulphuric acid of the hyposulphate. From that, the quantity of the latter acid is calculated, which indicates also that of the water of crystallisation.

#### DETERMINATION OF HYPOSULPHUROUS ACID AND OF ITS SALTS.

\* When hyposulphites in the solid form have to be analysed, they must, like the dry hyposulphates, be cautiously oxydised by means of fuming nitric acid. The oxydised mass is diluted by water. If a little sulphur has been liberated, it is collected in a filter and determined separately. A solution of baryta-salt is then poured in the liquor to precipitate the sulphuric acid, from which that of the hyposulphurous acid is calculated.

\* When the oxydisation of the hyposulphite is effected by fusion with nitrate or chlorate of potash, the operator must use greater caution still than for the oxydisation of the sulphites and hyposulphates by these salts, for the reaction is much more violent. The nitrate or chlorate of potash, to which carbonate of potash or of soda has been added, is intimately mixed with the hyposulphite in a platinum crucible, and a layer of the oxydising mixture is further put over the whole. After fusion, the mass is treated by water, muriatic acid, and a solution of chloride of barium, absolutely, as for the sulphites and hyposulphates which have been treated in the same manner.

\* But when a hyposulphite is contained in a solution, neither nitric acid, nor aqua regia, nor even chlorine gas, can convert the hyposulphurous acid into sulphuric acid in a safe manner, that is, without loss. The free acids which are poured in the solutions of the hyposulphites, transform the hyposulphurous acid into sulphurous acid, and into sulphur, which is deposited.

A pretty considerable time must elapse before the decomposition is finished, but there is always a chance, even though operating with chlorine gas, that a little sulphurous acid will have volatilised, which accident is especially to be feared when the stream of chlorine gas is too slow ; wherefore it is better to resort to another method for separating hyposulphurous acid from its neutral solutions.

\* The best process is the following:—The solution of the hyposulphite is mixed with a pretty large excess of a solution of neutral nitrate of silver. The whole is then heated. The hyposulphurous acid is thereby decomposed, half of its sulphur absorbs all the oxygen of the acid, and that of the portion of oxyde of silver which is decomposed ; it is thereby converted into sulphuric acid, which remains in solution in the state of sulphate of silver ; the other half of the sulphur combines with the silver reduced, and is precipitated under the form of black sulphuret of silver. This sulphuret is collected on a filter, well washed, preferably with hot water, because sulphate of silver is only sparingly soluble. A solution of nitrate of baryta, which must be perfectly free from chloride of barium, is poured in the filtered liquor, which produces a precipitate of sulphate of baryta, from the quantity of which that of the hyposulphurous acid may already be calculated, since the sulphuric acid produced during the operation contains half the sulphur which existed in the whole of the hyposulphite. The quantity of the hyposulphurous acid might also be estimated from the quantity of that of the sulphuret of silver, since this substance contains half of its sulphur.

\* In this process of analysing it is necessary that the solution of nitrate of silver employed should be dilute, in order that the liberated nitric acid should not have an oxydising action upon the sulphuret of silver produced. This precaution is so much the more necessary, that, in order to hasten the decomposition, it is necessary to heat the whole. Now, if the nitric acid set at liberty should come to part with any oxygen, the quantity of

and the operator calculates the quantity of hyposulphuric acid necessary to saturate it.<sup>1</sup>

The analysis is performed in the same manner, when the liquor contains, besides sulphuric acid, that combination of sulphuric acid and ether, known under the name of sulphovinic acid, and which, by its properties, bears some analogy with hyposulphuric acid.

If, however, the sulphuric and hyposulphuric acids are combined with bases, the best way of determining their respective quantities consists in analysing two portions of the combination. In one of these portions the quantity of the sulphuric acid is determined in the usual way, that is to say, by adding a solution of baryta-salt to the liquor, and from the weight of the sulphate of baryta produced, the quantity of the sulphuric acid which it contains is calculated. The other portion of the combination is treated by sulphuric acid, by aqua regia, by nitrate of potash or chlorate of potash, in order to transform the hyposulphuric acid into sulphuric acid, as was said before. When the operation is terminated, the sulphuric acid is precipitated by means of a baryta-salt, and its quantity is determined; the difference between the two quantities of the sulphuric acid obtained in the two experiments indicates the quantity of sulphuric acid which has been produced by the oxydisation of the hyposulphuric acid, from which the quantity of the latter may then be easily calculated.

\* When a combination contains sulphates and sulphites, the quantities of the two acids may be determined in the same manner, except that in order to determine the quantity of the sulphuric acid, the solution must be acidified with muriatic acid before proceeding to precipitate it.

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<sup>1</sup> It is hardly necessary to remark, that it is only the free baryta which is thus precipitated as carbonate, the hyposulphate of that base remaining in solution or in a soluble state is afterwards precipitated by sulphuric acid as described.—Ed.

The following note is by M. E. Peligot:—

\* The researches which have been lately made upon the oxacids of sulphur having established six varieties of these compounds (page 212, vol. i.) have augmented the difficulties with which their separation is fraught, when existing simultaneously. According to Messrs. Fordos and Gélis, the following method should be resorted to for the purpose of analysing an aqueous solution of a mixed compound consisting of a sulphate, sulphite, hyposulphite, hyposulphate, and bisulphuretted hyposulphate.

The liquor must be divided into four equal portions.

*First portion.*

\* This portion is devoted to the determination of the sulphuric acid, and in order to do this an excess of solution of chloride of barium is poured into the non-acidified liquor; the precipitate being collected on a filter is washed thereon, first, with boiling distilled water; secondly, with water slightly acidified with muriatic acid; the precipitate is afterwards dried and ignited with the ordinary precautions.

*Second portion.*

\* This second portion must be treated by iodine, the action of which is 1st. To transform the sulphurous into sulphuric acid, owing to the decomposition of the water, hydriodic acid being produced at the same time. 2nd. To transform the hyposulphite into bisulphuretted hyposulphate and iodide of alkali, each equivalent of hyposulphite absorbing half an equivalent of sulphur without formation of either sulphurous or sulphuric acid, or deposit of sulphur. Before adding the iodine it is necessary to hold in suspension in the liquor a few grammes of carbonate of magnesia, in order that at the moment when the hydriodic acid will be formed, it may find a base which it may at once saturate, and thus be prevented from acting as an acid upon the as yet undecomposed portion of sulphite or of hyposulphite contained in the liquor, which would cause a disengagement of sulphurous acid, and a deposit of sulphur.

\* The liquor, after this addition, being saturated with iodine, the operator takes care to note the weight of the iodine employed, and the quantity of sulphuric acid which it contains is again determined by chloride of barium; the difference between the weight of the sulphate of baryta yielded by this operation and that which was given by the first liquor, indicates the quantity of sulphurous acid, and also that of the iodine which has been employed to transform it into sulphuric acid.

\* Deducting now from the total weight of the iodine employed that which has served to transform the sulphurous acid into sulphuric acid, the operator thus finds the quantity of iodine which has been absorbed by the hyposulphurous acid, and, consequently, the weight of the latter.

\* For the purpose of treating the liquor by iodine, the operator should employ either an alcoholic solution of iodine recently prepared, and of a known strength, or of small fragments of iodine taken from a phial, the weight of which shall have been previously determined.

\* This solution takes place rapidly, and it is easy to hit the point of saturation; the operator must stop as soon as the liquor assumes a yellow tinge.

#### *Third portion.*

\* This third portion is devoted to the determination of the bisulphuretted hyposulphuric acid. The liquor is treated by iodine to saturation, and with the same precautions as above, only it is not necessary to note the quantity of iodine employed; the iodine will form, as we have said, a sulphate at the expense of the sulphite, and a bisulphuretted hyposulphate at the expense of the hyposulphite. This being done, the saline solution must be diluted with water, and a current of chlorine gas is passed through it, which will transform into sulphuric acid all the sulphur of the bisulphuretted hyposulphate, without acting upon the ordinary hyposulphate. When the saturation is completed, the liquor is saturated by chloride of barium. The weight of the sulphate of baryta obtained represents the sulphur of the sulphate, of the sulphite, of the hyposulphite, and of the



bisulphuretted hyposulphate. The experiments performed with the first and the second portion of the liquor give the weight of the sulphur contained in the three first of these salts, the difference betwixt this weight and that of the last operation indicates the quantity of sulphur contained in the bisulphuretted hyposulphate.

\* The sulphate of baryta obtained in this last operation, is mixed with a large proportion of iodate of baryta, due to the action of chlorine upon the iodides contained in the liquor. This salt being very sparingly soluble in water, the washing of the sulphate of baryta must be continued for a long time in order to eliminate it entirely.

*Fourth portion.*

\* There remains only to determine the quantity of the hyposulphuric acid. To arrive at this, it is sufficient to know the weight of all the sulphur contained in the liquor. Messrs. Fordos and Gélis recommend to add a little caustic soda to the solution, and to evaporate it to dryness. The solid residuum is then treated by fuming nitric acid, in order to convert all the sulphur into sulphuric acid.

\* It is preferable, it would seem, to mix the residuum with its own weight of pure and dry nitre, and to ignite it. The product, after being kept in a state of fusion for some time, is saturated by nitric acid, and then treated by chloride of barium, which will precipitate all the sulphur contained in the solution in the state of sulphate of baryta.

## CHAPTER XLIII.

## PHOSPHORUS.

## DETERMINATION OF PHOSPHORIC ACID.

WHEN phosphoric acid exists in solution in a liquor which contains nothing else but nitric acid, it may be determined in the same manner as arsenic acid, with which it has much analogy in respect to its properties. A known weight of pure and recently ignited protoxyde of lead is added to the solution, which is then evaporated to dryness, and the residuum is ignited in a small counterpoised platinum capsula. The quantity of the dry phosphoric acid is then found by deducting from the weight of the fused mass that of the protoxyde of lead which has been added.

The determination of phosphoric acid requires also that the solution should contain no acid which may form with protoxyde of lead a salt incapable of being reduced into pure protoxyde of lead by ignition.

\* The quantitative determination of phosphoric acid may also be performed by means of metallic iron by the method which Berthier indicated for the estimation of arsenic acid, and which I have explained (page 337). The advantage of this method is that it can be employed in several cases in which the use of protoxyde of lead is impracticable. When this method is used, the presence of nitric acid or muriatic acid, or sulphuric acid, and even of fixed alkalies is not objectionable. As phosphoric acid cannot, like

arsenic acid, be determined quantitatively by sulphuretted hydrogen, Berthier's method is still more useful for the determination of phosphoric acid than for that of arsenic acid. Rather less than one part of metallic iron for two parts of the phosphoric acid suspected in the liquor is employed. As for the determination of arsenic acid, an excess of peroxyde of iron far from being objectionable is, on the contrary, an advantage. If too little solution of the persalt of iron is poured in the liquor, so that a basic perphosphate of iron is formed, the ammonia dissolves some of the perphosphate of iron.<sup>1</sup>

\* If phosphoric acid is contained in an acid solution, uncombined with bases, or, which is worse still, if it is combined with earths or metallic oxydes, it cannot be quantitatively determined in the state of ammonio-magnesian phosphate by adding to the liquor, previously supersaturated with ammonia, a solution of sulphate of magnesia previously mixed with a sufficient quantity of a solution of muriate of ammonia to prevent the ammonia from producing a precipitate in it; it is true that, in presence of phosphoric acid, a precipitate of ammonio-magnesian phosphate is produced, but this salt is insoluble only in an excess of phosphates, so that it is not entirely precipitated when the salt of magnesia is in excess. Thus, though the method of determining magnesia quantitatively by a solution of phosphate of alkali with addition of ammonia is good, a magnesian salt cannot be employed inversely for the purpose of determining phosphoric acid, for the results which are thus obtained are quite inaccurate. We have said, in the first volume of this work, that the use of a magnesian salt is very suitable in qualitative analysis for detecting the presence of phosphoric acid, especially when sulphuric acid exists simultaneously with it.

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<sup>1</sup> The operator knows that he has employed a sufficient quantity of the solution of pernitrate of iron, because in that case the precipitate produced by the excess of ammonia will be reddish-brown, in the contrary case, it will be white or whitish.—En.

The separation of phosphoric acid from other substances is also attended sometimes with the greatest difficulties. The most accurate manner of determining its quantity in the analysis of phosphates, consists in taking a given weight of the combination, and to determine only the bases or substances which are combined with the phosphoric acid, and to look upon the loss as indicative of the latter.<sup>1</sup>

#### DETERMINATION OF PHOSPHOROUS AND HYPOPHOSPHOROUS ACIDS.

Phosphorous and hypophosphorous acids may be quantitatively determined in a liquor by a method analogous to that employed for phosphoric acid. To the solution, a known weight of protoxyde of lead is added, and also as much nitric acid as is necessary to convert the phosphorous acid or hypophosphorous acid into a higher degree of oxydisation. The whole being then reduced into a smaller bulk by evaporation, it is poured in a counterpoised platinum capsula, and evaporated to dryness; the dry mass is then ignited, and its weight determined. The residuum consists of phosphoric acid and protoxyde of lead. Deducting therefrom the weight of the protoxyde of lead employed, the remainder indicates the quantity of phosphoric acid, from the weight of which the quantity of the phosphorous and hypophosphorous acids are calculated.

The complete oxydisation of the phosphorous and hypophosphorous acids are principally produced, during the ignition, by the nitrate of lead which has been formed during the experiment. The ignition must be performed with care, because the mass intumesces, and a loss might thus be sustained. On the other

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<sup>1</sup> Another method has lately been proposed by M. Raewsky for the estimation of phosphorus, which method consists in converting it into perphosphate of iron, which is insoluble in acetic acid, washing the precipitate thoroughly, and dissolving it in muriatic acid, bringing the liquor to the minimum by sulphate of soda, and converting it into a protosalt by means of a solution of permanganate of potash of a known strength, and which we have already described before, (page 114). M. Raewski has ascertained that the perphosphate of iron has always the same composition, namely,  $\text{PO}_5$ ,  $\text{Fe}_2\text{O}_3$ , so that the phosphorus or phosphoric acid may be calculated from the quantity of the iron obtained by the above process.—ED.

hand, an incautious management of the heat might also cause a loss, if too large a proportion of protoxyde of lead has been employed, because too much nitrate of lead would then be formed, which would strongly decrepitate before being decomposed.

\* Phosphorous and hypophosphorous acids cannot be converted into phosphoric acid by nitric acid, except in very concentrated solutions, and with the help of heat. Wherefore, when the operator wishes to determine them quantitatively, by means of metallic iron according to Berthier's method, it is necessary, after having added the nitric acid, to evaporate the liquor to a very small bulk. Yet it may very easily happen that a small quantity of the phosphoric acid produced is volatilised by the action of the heat. This effect does not take place when, besides nitric acid, the operator adds nitrate of potash to the liquor, and evaporates the whole to dryness. The oxydised mass may then be dissolved in water, supersaturated with nitric or muriatic acid, and the phosphoric acid produced determined by means of metallic iron.

\* It is advisable, for the purpose of determining phosphorous and hypophosphorous acids, to employ this method only when the liquor contains muriatic acid, sulphuric acid, or alkalies, in which case that which consists in the use of protoxyde of lead cannot be resorted to. Otherwise, that is if the substances just enumerated are absent, the latter method is preferable.

#### SEPARATION OF PHOSPHORIC ACID FROM SULPHURIC ACID.

Phosphoric acid may be very accurately separated from sulphuric acid by means of a solution of a salt of baryta, an excess of which, poured in an acid solution, precipitates only sulphate of baryta, the phosphate of that base remaining in solution in the liquor. From the weight of the sulphate of baryta, that of the sulphuric acid which it contains is calculated. The operator may then determine in the filtered liquor the quantity of the phosphoric acid which it contains, by saturating the solution with

ammonia, which produces a precipitate of phosphate of baryta; but this method does not yield very accurate results. The phosphate of baryta is not completely precipitated by the supersaturation with ammonia, a small quantity of this salt remains in solution, which is so much the more considerable that the liquor is more acid, because a greater quantity of ammoniacal salt is then produced, which dissolves a little phosphate of baryta. The quantity of phosphate of baryta which is not precipitated is pretty considerable, especially when the solution contains free muriatic acid. Phosphate of baryta is so soluble in a solution of muriate of ammonia, that a solution of chloride of barium, added to a solution of phosphoric acid containing much muriatic acid, and subsequently supersaturated with ammonia, often fails in precipitating the smallest trace of phosphate of baryta.

\* In such a case, the best method of determining quantitatively phosphoric acid in the liquor, is, after having removed the sulphuric acid, to employ iron, according to Berthier's method, but the operator must then take care to eliminate the excess of baryta contained in the liquor, by means of sulphuric acid.

#### SEPARATION OF PHOSPHORIC ACID FROM THE ACIDS OF ARSENIC, FROM SELENIUM, AND FROM TELLURIUM.

Phosphoric acid may be very accurately separated from the acids of arsenic, by passing a current of sulphuretted hydrogen through the acid liquor; this reagent precipitates only the acids of arsenic in the state of sulphuret of arsenic, whilst it has no action upon phosphoric acid. The quantity of the arsenic acid is then determined from the weight of the sulphuret of arsenic obtained in the manner spoken of (page 332.) If the operator wishes to estimate the phosphoric acid contained in the liquor filtered from the sulphuret of arsenic, protoxyde of lead may be resorted to in the manner described before. Yet the solution must not, of course, contain any other substance than nitric acid, and the absence of all acids capable of forming with protoxyde of lead salts which would resist the action of the fire,

must have been previously ascertained. It is necessary also to expel beforehand even the slightest trace of sulphuretted hydrogen which might remain in solution.

\* The determination of phosphoric acid is more easily effected, however, in such cases, by metallic iron than by protoxyde of lead, because the action of nitric acid upon sulphuretted hydrogen is to form a little sulphuric acid, the presence of which renders the determination of phosphoric acid by protoxyde of lead uncertain in its results.

The method which serves to separate phosphoric acid from the acids of arsenic might be likewise employed for separating it from tellurous and from selenious acids, when these substances exist simultaneously with it in a compound: but in such a case the separation is effected much better by sulphurous acid. Selenic acid may be separated from phosphoric acid by the same process which is used for separating the latter from sulphuric acid, that is to say, by means of a solution of baryta-salt, for which purpose nitrate of baryta should be chosen. But, if muriatic acid has been added to the solution, the whole must be heated with an excess of this acid, in order to convert the selenic acid into selenious acid, which is precipitated afterwards by sulphurous acid. If telluric acid were present, it should be first converted into tellurous acid, and afterwards reduced by sulphurous acid.

#### SEPARATION OF PHOSPHORIC ACID FROM VANADIC ACID.

\* In order to separate these two acids from each other, they must be first combined with ammonia: the excess of volatile alkali is expelled by applying heat, and to the solution the operator adds a solution of muriate of ammonia, in which vanadate of ammonia is insoluble. This latter salt is washed with a solution of muriate of ammonia, and it is subsequently converted into vanadic acid by heating it moderately in contact with the air. The phosphoric acid is afterwards determined in the liquor filtered from the vanadate of ammonia.

SEPARATION OF PHOSPHORIC ACID FROM THE OXYDES OF ANTIMONY, OF TIN, OF GOLD, OF MERCURY, OF SILVER, OF COPPER, OF BISMUTH, OF LEAD, AND OF CADMIUM.

When phosphoric acid is combined with these oxydes, a certain quantity of the combination is to be weighed, and dissolved in an acid; in most cases muriatic acid is preferred for the purpose. The only cases in which this acid cannot be employed are those in which the combination contains either protoxyde of lead or oxyde of silver. The solution is first diluted with water, and the oxyde is precipitated by a current of sulphuretted hydrogen. The metallic sulphuret thus obtained is treated according to the methods which have been described before, and the quantity of the oxydes determined. It is best to infer the quantity of the phosphoric acid from the loss, but this acid may also be determined by means of metallic iron after previously expelling the slightest traces of sulphuretted hydrogen.

When phosphoric acid is combined with oxyde of silver, or with protoxyde of lead, another method may be adopted. The combination is dissolved in nitric acid, which is the only acid which can be employed in this case, and the oxyde of silver is precipitated from the solution by means of muriatic acid. From the quantity of chloride of silver obtained, that of the oxyde of this metal is calculated, and subsequently that of the phosphoric acid, unless the operator wishes to determine the latter by means of metallic iron.

If protoxyde of lead is contained in the solution, it should be precipitated therefrom by sulphuric acid, alcohol being added to the liquor, by which means the sulphate of lead is precipitated completely, because it is altogether insoluble in a spirituous liquor. It should be washed with alcohol. From the weight of the sulphate of lead obtained, that of the protoxyde of lead is calculated, and the quantity of the phosphoric acid is afterwards estimated from the loss.



SEPARATION OF PHOSPHORIC ACID FROM ARSENIC ACID, AND  
FROM THE OXYDES ABOVE NAMED.

When the substance to be analysed is composed of phosphoric acid, of arsenic acid, and of one of the oxydes above named—which can be precipitated completely from an acid solution by sulphuretted hydrogen, which combinations occur in nature, and in which phosphoric and arsenic acids, being isomorphous, may replace each other in the most varied proportions—the analysis may be performed by two different methods.

The combination is dissolved in an acid, for which purpose muriatic acid is ordinarily chosen ; but, in certain cases, nitric acid answers better.

One of the methods consists in diluting the solution with a sufficient quantity of water, and precipitating the oxyde in the state of sulphuret, by means of sulphuretted hydrogen. The sulphuret of arsenic, and the metallic sulphuret are afterwards separated from each other, and the quantity of the metallic oxyde and of the arsenic acid are afterwards determined.

In the other method, the acid solution is supersaturated with ammonia, and hydrosulphuret of ammonia is added thereto in sufficient quantity only to precipitate the oxyde in the state of sulphuret. The liquor is then filtered, and the sulphuret of arsenic is afterwards precipitated therefrom by adding dilute muriatic acid, or acetic acid. The substance, in that case, must not contain oxyde of antimony, or of tin, because the sulphurets of these two metals are, like that of arsenic, soluble in an excess of hydrosulphuret of ammonia. Having already indicated the precautions, which it is absolutely necessary to take in analyses of that kind, they need not be related again here. When the operator has found the quantity of the arsenic acid, and that of the metallic oxyde, the quantity of the phosphoric acid is calculated from the loss, this latter acid not being acted

upon by either sulphuretted hydrogen, or hydrosulphuret of ammonia.

The analytical process is the same when the combination consists of phosphoric acid, of arsenious acid, and of one of the metallic oxydes which have been mentioned.

SEPARATION OF PHOSPHORIC ACID FROM THE OXYDES OF  
COBALT, OF ZINC, OF IRON, AND OF MANGANESE.

When phosphoric acid is combined with these metallic oxydes, the best method of analysing the combination is the following :—A certain weight of the compound is dissolved in an acid—muriatic acid answers best for this purpose—the solution is supersaturated with ammonia, and the oxydes are afterwards precipitated in the state of metallic sulphuret by hydrosulphuret of ammonia. When the muriatic acid solution of these metallic phosphates is saturated with ammonia, the phosphate precipitates first, but sometimes also it redissolves in the excess of the ammonia. But, even when the phosphate remains precipitated, it is decomposed in a complete manner by digestion with hydrosulphuret of ammonia, so that the metallic sulphuret precipitated is entirely free from phosphoric acid. From the quantity of metallic sulphuret thus obtained, that of the metallic oxyde contained in the solution is determined by the methods which have been described before. The loss indicates the quantity of the phosphoric acid.

\* The combinations of phosphoric acid with the oxydes of cadmium, of lead, of bismuth, of copper, of silver, and of mercury, may be analysed in the same manner. But this method should not be applied to the combinations of phosphoric acid with the oxydes of silver, and of lead; those which I have indicated previously for the quantitative determination of these compounds being more simple.

SEPARATION OF PHOSPHORIC ACID FROM THE OXYDES OF  
URANIUM, AND OF NICKEL.

The analysis of the combinations of phosphoric acid with the metallic oxydes which, like those of uranium and of nickel, cannot be precipitated from an acid solution by sulphuretted hydrogen, or which are imperfectly precipitated from an ammoniacal solution by hydrosulphuret of ammonia, are attended with more difficulties. The combination of phosphoric acid with oxyde of nickel, might be dissolved in muriatic acid, and ammonia being added to the solution, the oxyde might then be precipitated in the state of sulphuret of nickel by hydrosulphuret of ammonia; but the operation, as we said, (page 146), is attended with difficulties. This method is not appropriate either for analysing the combination of phosphoric acid with oxyde of uranium. Consequently, when the quantity of these metallic oxydes has to be determined in such a combination, the following process should be adopted:—A certain portion of the compound is weighed, and then mixed in a large platinum crucible with about three times its weight of dry carbonate of potash, or of soda; the whole is ignited, and the ignited mass is then to be treated by water, which dissolves the phosphate of alkali produced and the excess of alkaline carbonate employed, whilst the metallic oxydes remain behind. These oxydes are washed with water, and their weight is determined. The quantity of phosphoric acid which was combined with them is indicated by the loss.

The metallic oxydes which water has not dissolved, should always be dissolved in muriatic acid, and subsequently precipitated from that solution, because they ordinarily contain a pretty considerable quantity of alkali from which they cannot be freed by washing, which is especially the case when this method has been employed to separate peroxyde of uranium from phosphoric acid. The uranium remains united with the alkali in the state of combination. It must therefore be dissolved in muriatic acid, and precipitated therefrom by ammonia; the

precipitate is afterwards washed with a solution of muriate of ammonia, ignited, and then weighed.

Berzelius employed this method for separating phosphoric acid from peroxyde of uranium, in the mineral called uranite.<sup>1</sup>

\* Phosphoric acid may be separated from metallic oxydes in several phosphates, by fusing the latter with an excess of carbonate of alkali, when the oxydes are completely insoluble, both in carbonate of alkali, and in pure alkali. This method may also be employed when phosphoric acid has to be separated from the oxydes of iron, of zinc, of cobalt, of copper, and some other metals. The advantage of this method is, besides, that the phosphoric acid may be determined by means of iron in the alkaline solution, after having previously supersaturated it by an acid. It is better however, in most cases, to precipitate the metallic oxydes by means of sulphuretted hydrogen, or of hydrosulphuret of ammonia, this method of analysis being more accurate, and less difficult.

#### SEPARATION OF PHOSPHORIC ACID FROM THE OXYDES OF CHROMIUM.

\* This separation is attended with difficulties. If the solution is neutral, the phosphoric acid is separated from the chromic acid by means of a solution of chloride of calcium which precipitates the phosphoric acid in the state of phosphate of lime,

<sup>1</sup> Uranite (calcareo-phosphate of uranium) is found chiefly at St. Symphonia, near Antrim, and at St. Yrieux, near Limoges, in France, and in several places in Saxony. That of Austria, analysed by Berzelius, was found to consist of

Peroxyde of Uranium . . . . .	59.37
Phosphoric acid . . . . .	14.63
Lime . . . . .	5.66
Magnesia, and Oxyde of Manganesc. . . . .	0.19
Silica, and Oxyde of Iron . . . . .	2.85
Baryta . . . . .	1.51
Water . . . . .	14.90
Fluoric Acid, and Ammonia . . . . .	Traces.

but does not precipitate the chromic acid. The phosphate is collected on a filter, washed, ignited, and the weight is determined. In most cases, this precipitate is a neutral phosphate of lime, from the weight of which the quantity of the phosphoric acid may be calculated. It is better, however, to determine the quantity of this acid by direct experiment, especially when the solution from which it was precipitated, instead of being neutral, was acid, the operator having consequently been obliged to neutralise it with ammonia. The method by means of which, the quantity of phosphoric acid existing in the phosphate of lime is determined, will be exposed farther on.

\* An acid solution from which phosphoric acid has to be separated from chromic acid, should first be saturated by ammonia, after which a solution of chloride of calcium is poured into it. If the solution have been supersaturated with a little ammonia, it must be filtered rapidly, out of the contact of the air, in order that the phosphate of lime should not be contaminated by carbonate of lime.

\* If the solution be alkaline, and if it contain an alkaline carbonate, it should first be supersaturated by nitric acid, and left at rest for a long time, and which is better in a moderately warm place, in order that all the carbonic acid may be completely disengaged. It is saturated afterwards with ammonia, and then mixed with a solution of chloride of calcium.

\* After having separated the phosphate of lime by filtering, the filtered liquor is evaporated to dryness, and the residuum, if it contains any ammoniacal salts, is ignited; it is then mixed with carbonate and nitrate of alkali, and the fused mass is treated as has been said (page 328).

\* The separation of phosphoric acid from oxyde of chromium might be effected by fusing the combination with hydrate and nitrate of potash, in order to convert the oxyde of chromium which it contains into chromic acid, which might afterwards

be separated from phosphoric acid by the means which I have indicated. The separation of oxyde of chromium and of phosphoric acid by fusion with carbonate of potash or of soda, might be performed in the same manner as that of oxyde of nickel, of oxyde of uranium, and other oxydes which are insoluble in solutions of carbonates of alkalies, were it practicable to effect the fusion out of the contact of the air, by the action of which a portion of the oxyde of chromium would be converted into chromic acid, and which, upon the mass being subsequently treated by water, would be dissolved along with the phosphate of alkali.

#### SEPARATION OF PHOSPHORUS FROM THE METALS.

\* When phosphorus is combined with metals capable of being precipitated from their solutions by sulphuretted hydrogen or by hydrosulphuret of ammonia, nitric acid or aqua regia is poured upon the combination, and the whole is heated. The phosphuret dissolves completely, even when it contains much phosphorus, and without leaving a trace of the latter substance. The solution is treated in the same manner as an acid solution of a metallic phosphate. There are, however, only a small number of metals which combine with phosphorus, so as to form phosphurets. Copper, chromium, iron, nickel, and cobalt are about the only metals which can thus unite with phosphorus in a great number of various proportions.

\* Muriatic acid, even with the help of heat, has no action upon the metals which decompose water under the influence of an acid, such as iron, nickel, and cobalt.

\* The phosphurets of the metals just named, may very well be decomposed like the arseniurets of the same metals, by fusing them in the pulverised state, with nitrate and carbonate of alkali (page 343).

## SEPARATION OF PHOSPHORIC ACID FROM YTTRIA.

The separation of phosphoric acid from the non-alkaline earths, is often attended with extraordinary difficulties. Phosphoric acid produces, with these substances, compounds which have so much resemblance with the pure earths, that it has often happened, even to distinguished chemists, to overlook a very considerable quantity of this acid in quantitative analyses.

Phosphoric acid forms with yttria a compound which occurs in nature. To separate these two substances from each other Berzelius proceeds as follows :—The combination is fused with carbonate of soda, and the fused mass is treated by water, which dissolves the phosphate and the carbonate of soda, and leaves the yttria behind.

## SEPARATION OF PHOSPHORIC ACID FROM ALUMINA.

The separation of phosphoric acid from alumina is very difficult. Phosphate of alumina behaves towards a solution of potash much in the same manner as alumina. Neither can phosphoric acid be separated from alumina by fusion with carbonate of soda, because phosphate of alumina is soluble in a concentrated solution of the latter salt.

According to Berzelius, the analysis of this compound may be performed as follows :—The quantity of the compound which it is intended to submit to analysis is first reduced into fine powder, and weighed. It is then mixed in a platinum crucible with silicic acid in extremely fine powder, and with carbonate of soda, and the mixture is exposed for half an hour to a red heat. If the combination contains hardly any thing else but phosphoric acid and alumina, the mixture should consist of two parts of phosphate, and one and a half of silicic acid, and about six of carbonate of soda. The pure silicic acid, obtained from the analysis or silicious compounds, is the best suited to the purpose, but should the operator have none, rock-crystal reduced into very fine powder by levigation, answers the same purpose. The

ignited mass is digested in water ; that which refused to dissolve is separated by filtering, and washed with water. The solution contains phosphate of soda, and the excess of carbonate of soda. The residuum consists of silicic acid combined with alumina and soda. A small quantity of silicate of soda has dissolved also ; in order to precipitate it, a little carbonate of ammonia is added to the solution, and the whole is left to digest. The slight precipitate which is then produced is added to the mass which water refused to dissolve. Muriatic acid is poured on the latter, and the whole is evaporated to perfect dryness in a capsula of porcelain or of platinum, which renders the silicic acid insoluble. This being done, the dry mass is to be thoroughly drenched with muriatic acid, and after some time water is poured upon it. The whole of the silicic acid employed remains in an insoluble state, the alumina on the contrary has dissolved, and is precipitated from the filtered liquor by carbonate of ammonia. If other bases are present they have dissolved with the alumina. The quantity of the phosphoric acid is generally estimated from the loss, when the combination contained no other acid capable of forming a soluble salt with soda. If, however, the operator wishes to determine immediately the quantity of the phosphoric acid as accurately as possible, methods should be employed, which will be described farther on.

The method employed by Fuchs to separate phosphoric acid from alumina, is as follows : A certain quantity of the combination is weighed and dissolved in a solution of pure potash, and a solution of silicate of potash (liquor silicum) is added thereto. A thick mucilaginous mass is thus obtained, which is diluted with water, and afterwards heated to ebullition, by which an abundant precipitate of silicate of alumina and potash is formed. This precipitate is treated by muriatic acid, after which the jelly produced by the silicic acid is evaporated to dryness, and the latter is separated in the same manner as in Berzelius' method. The alumina is afterwards precipitated from the filtered liquor. The liquor filtered from the silicate of alumina



and potash contains the whole of the phosphoric acid which existed in the compound.

#### SEPARATION OF PHOSPHORIC ACID FROM MAGNESIA.

In order to separate phosphoric acid from magnesia, the combination is fused with carbonate of potash or of soda, and the ignited mass is treated by water, which dissolves the phosphate of alkali and the excess of the alkaline carbonate, and leaves the magnesia.

#### SEPARATION OF PHOSPHORIC ACID FROM LIME, STRONTIA, AND BARYTA.

The separation of phosphoric acid and of these earths is not difficult, and yields very accurate results. A certain quantity of the combination is weighed and dissolved in an acid, preferably in muriatic acid. If the phosphoric acid is combined with baryta only, the acid solution is diluted with water, and sulphuric acid is added thereto in order to precipitate the baryta. From the weight of the sulphate of baryta obtained, the quantity of the baryta is calculated, and that of the phosphoric acid is deduced from the loss.

When, on the contrary, phosphoric acid is combined with strontia or with lime, weak alcohol is added to the muriatic acid solution, and sulphuric acid being added, precipitates the earths in the state of sulphates, which are insoluble in weak alcohol, so that they may thus be completely separated from the solution. They are then washed with weak alcohol and ignited. After ignition, their weight is determined, from which the quantity of the strontia or of the lime is calculated; that of the phosphoric acid is estimated from the loss.

\* The acid combinations of phosphoric acid with baryta, strontia, and lime, are insoluble in muriatic acid after ignition. They can be decomposed only by boiling them for a pretty long time in the pulverised state with concentrated sulphuric acid, in

a platinum capsula. When the decomposed mass has cooled, it is treated with a moderate quantity of water, which does not dissolve the sulphate of baryta. If the combination contains strontia or lime, weak alcohol is poured on the mass which has been decomposed by sulphuric acid, and the sulphate produced being insoluble in this menstruum, it is washed with it. I have already said before, that phosphate of lead might be analysed in the same manner.

The combinations of phosphoric acid with the alkaline earths may be analysed by fusing them in a platinum crucible, with three times their weight of carbonate of potash or of soda. The fused mass is treated by water, which dissolves the earth in the state of carbonate and free from phosphoric acid. The solution contains phosphate of alkali and the excess of alkaline carbonate employed.

#### SEPARATION OF PHOSPHORIC ACID FROM POTASH AND SODA.

When phosphoric acid is combined with these two alkalies, the best method of determining it quantitatively consists, according to Mitzcherlich, in determining the quantities of the bases, and estimating that of the phosphoric acid from the loss. A certain quantity of the combination is weighed, dissolved in water, and an excess of a solution of acetate of lead is added to the solution. The phosphoric acid combines with the protoxyde of lead, and is completely precipitated, even when the combination submitted to analysis is an acid phosphate, because the precipitate is almost insoluble in acetic acid. This precipitate is collected on a filter. A current of sulphuretted hydrogen might be passed through the filtered liquor, in order to precipitate the protoxyde of lead in the state of sulphuret of lead; but a better and less complicated method consists in pouring a solution of carbonate of ammonia in the liquor, and heating the whole. The excess of the protoxyde of lead employed is then precipitated in the state of carbonate of lead. The liquor filtered from this salt is evaporated to dryness, and the

residuum is ignited. The weight of the carbonate of alkali obtained is then determined ; if this cannot be done with great accuracy, which is the case, for example, when the substance is carbonate of potash, it is treated by muriatic or by sulphuric acid, and from the weight of the metallic chloride, or of the sulphate of alkali, the quantity of alkali which existed in the phosphate is determined ; that of the phosphoric acid is estimated from the loss.

It is not so advantageous to employ chloride of barium instead of acetate of lead to precipitate a phosphoric acid. Phosphate of baryta is not absolutely insoluble in water, and its solubility is much increased when the phosphate submitted to analysis being an acid phosphate, the operator is obliged to add ammonia in order to dissolve it. The excess of baryta employed cannot be so well removed by carbonate of ammonia as by sulphuric acid ; and if precipitated by sulphuric acid, and ammonia has been previously added to the solution of the phosphate, sulphate of ammonia is produced at the same time, which cannot be expelled completely from the sulphate of a fixed alkali without loss.

\* The neutral combinations of phosphoric acid with potash and with soda, are, after ignition, more easy to analyse. A solution of nitrate of silver is added to the solution. A white precipitate of neutral phosphate of silver is thus obtained, which is collected on a filter and dried ; it may subsequently be fused, as for chloride of silver, and its weight determined, from which that of the phosphoric acid is estimated. It may be also decomposed, after fusion, by nitric acid, and precipitated afterwards by muriatic acid, so as to determine the oxyde of silver in the solution in the state of chloride of silver, which is a still better way of determining the phosphoric acid (page 193). The liquor filtered from the phosphate of silver must now be freed, first from the excess of oxyde of silver, by means of muriatic acid, and thus the quantity of the alkali in the solution, which contains nitric and muriatic acids, is then determined by means of the methods which have been described before.

\* It is not possible, however, to analyse thus the phosphates of potash and of soda which have not been ignited, and the solutions of which yield, when treated by nitrate of silver, a yellow precipitate of basic phosphate of silver. After the precipitation by the salt of silver, there remains a pretty large quantity of phosphoric acid in the liquor which has been filtered from this basic salt.

#### SEPARATION OF PHOSPHORIC ACID FROM LITHIA.

The separation of phosphoric acid from lithia is exceedingly difficult, especially when the combination contains soda besides. Berzelius employed the following process to decompose these combinations.

A certain portion of the compound is weighed, mixed, and fused in a platinum crucible, with twice its weight of carbonate of lime; the fused mass is carefully pulverised, and boiled with water. The liquor then contains lime and the whole of the alkalies, whilst the phosphate of lime remains insoluble. The liquor is then saturated with oxalic acid; the oxalate of lime which has formed is collected on a filter, the filtered liquid is evaporated to dryness, and the dry residuum is ignited. The alkaline carbonate thus obtained is calcined and weighed.

#### SEPARATION OF PHOSPHORIC ACID FROM SEVERAL BASES IN COMPLEX COMPOUNDS.

The analysis of the phosphates becomes very difficult when they simultaneously contain several bases which sulphuretted hydrogen or hydrosulphuret of ammonia cannot precipitate in the state of metallic sulphurets from acid or from neutral solutions, as, for example, when phosphoric acid is combined simultaneously with a metallic oxyde and with an earth. The analysis is then performed in the following manner:—A certain portion of the combination is weighed and ignited with carbonate of potash or of soda, and the calcined mass is then treated by

water. In most cases the water so added dissolves only the excess of alkaline carbonate employed and the phosphate of alkali produced. The bases with which the phosphoric acid was previously combined remain behind ; they are to be dissolved in muriatic acid, and separated by the methods which have been previously explained.

\* Of all the methods which may be employed to determine bases in the combinations of phosphoric acid, that which has been just described is unquestionably the best. It may be employed, as we have already said, for the analysis of all the simple or compound phosphates the bases of which are not dissolved by the alkaline carbonates, that is to say, for the analysis of the phosphates of alkaline earths and of most metallic phosphates ; but it cannot be resorted to, as we have already remarked, when phosphate of alumina is present. The determination of the phosphoric acid in the aqueous solution is effected, as will be shown farther on.

When the operator has to separate from each other the bases which exist in compounds containing phosphate of lime, or of protoxyde or of peroxyde of iron, Berzelius employs a method which was first proposed by Herschel to separate peroxyde of iron from other oxydes. The combination is dissolved in an acid, and, if the iron is in the state of protoxyde of iron, it is converted into peroxyde of iron by means of nitric acid or of chlorine gas. The liquor is then saturated by carbonate of ammonia as exactly as possible, or rather until a precipitate begins to appear, and then it is made to boil. The peroxyde of iron is thereby precipitated, while the phosphate of lime remains in solution. This method is grounded upon the fact that the neutral persalts of iron are precipitated from their solutions by ebullition. But as a small quantity of peroxyde of iron may still be kept in solution by a small quantity of free acid which may be present, the operator should add a little alkali to the filtered liquor, which should be boiled a second time until it has become too slightly acid to retain any peroxyde of iron. As the

precipitated peroxyde of iron always contains phosphoric acid, it should be dissolved in muriatic acid; the solution is then saturated by ammonia, and the peroxyde of iron is then precipitated therefrom in the state of sulphuret of iron by hydrosulphuret of ammonia. The liquor in which the lime is dissolved is concentrated by evaporation, and the lime is then precipitated by sulphuric acid and alcohol.

In general, in the analysis of the phosphates the operator must not forget that all the combinations—acid, neutral, and basic—of phosphoric acid are soluble in acids, but that a very large number of acid phosphates are not soluble in muriatic acid, in nitric acid, and in dilute sulphuric acid, after having been exposed to a red heat. In order to decompose these phosphates, a certain quantity thereof is to be weighed and fused with three times its weight of carbonate of potash or of soda, after which the fused mass is treated by water. The following method, which has already been indicated (page 440), is less complicated:—The insoluble compound is pulverised, and a weighed quantity of it is put in a platinum capsula, which must be pretty large, and concentrated sulphuric acid being poured upon it, the whole is boiled for a long time, taking care, however, not to volatilise all the excess of sulphuric acid. Water is then added with care; the combination dissolves then completely, provided the base of the phosphate is not one of those which form with sulphuric acid salts insoluble or sparingly soluble, such as, for example, protoxyde of lead, lime, strontia, and baryta.

In almost all the analysis of the combinations of phosphoric acid with the various bases which have been enumerated, hitherto we have not spoken of the method which should be adopted to determine immediately the quantity of this acid. The immediate determination cannot be effected as accurately as that of many other substances. The methods which consist in analysing in a precise manner the quantity of the base contained in the phosphates, and in calculating the quantity of the phosphoric

acid by the loss, yield unquestionably the most accurate results. Yet, in certain cases, and especially when the combination contains a great number of bases, it may be necessary or useful to determine immediately the quantity of the phosphoric acid.

After having separated the bases from the phosphoric acid by means of sulphuretted hydrogen, and heated for a long time the filtered acid liquor, in order to expel the slightest traces of sulphuretted hydrogen, it is customary to determine the quantity of the phosphoric acid in the following manner:—The liquor is saturated with ammonia, and the operator then adds the solution of a salt with the base of which phosphoric acid forms an insoluble compound. Acetate or nitrate of lead, or chloride of barium or of calcium are ordinarily chosen in preference. The solutions of the salts of lead are those which precipitate phosphoric acid best. When they are used, it is advisable to saturate the liquor exactly with ammonia. This liquor may, however, be slightly acid, provided this be owing to the presence of acetic acid, and provided the liquor contains no other acid. If solutions of salts of baryta are employed, the liquor must contain no muriatic acid. After having saturated the acid liquor by ammonia, the phosphoric acid may be precipitated by chloride of barium, or of calcium, but in that case the phosphate of baryta or of lime must be speedily collected on a filter and sheltered from the contact of the air during the filtering, because if this precaution was neglected it might be contaminated by some carbonate of baryta or of lime. I have already said before, that phosphate of baryta is not absolutely insoluble in a liquor which contains ammoniacal salts. As phosphate of lime appears to be less soluble in a liquor of that kind, the solution of chloride of calcium is generally preferred to that of chloride of barium, for the purpose of precipitating phosphoric acid. Berthier's method is, however, more suitable for the determination of the phosphoric acid in the liquor filtered from the metallic oxydes.

When the bases have been separated from the phosphoric acid by hydrosulphuret of ammonia, the liquor filtered from the

metallic sulphurets is acidified and heated until every trace of sulphuretted hydrogen has been expelled. The sulphur which has separated is then collected on a filter, and the phosphoric acid is precipitated in the manner mentioned above.

When the solution from which the phosphoric acid has to be precipitated contains carbonate of alkali or pure alkali, it must be acidified by adding acetic acid thereto, and left at rest for about twenty-four hours, covering it loosely so that all the carbonic acid may be disengaged. It is best to employ a flask capable of being covered, and into which the precipitation of the phosphoric acid, by the addition of chloride of calcium to the ammoniacal liquor is performed. The access of the air, and all formation of carbonate of lime is thus prevented. Time is allowed for the phosphate of lime produced to settle well at the bottom of the flask, the supernatant liquor is then filtered, the precipitate itself is afterwards thrown upon the filter and washed thereon.

\* When the combination has been fused with carbonate of alkali, and the fused mass has been afterwards treated by water, a solution of phosphate and of carbonate of alkali is always obtained (page 442).

It is always impossible to know exactly the composition of the precipitate which the salts of lead, chloride of barium, or chloride of calcium have produced in solutions of phosphates; wherefore the quantity of the phosphoric acid must never be calculated from the weight of such a precipitate. This is principally the case when chloride of barium or of calcium have been employed to precipitate phosphoric acid in the state of phosphate of baryta or of lime from a liquor which has been rendered ammoniacal; the precipitate consists, then, of a mixture of neutral and of basic salts in undetermined proportions. It is therefore absolutely necessary to estimate the quantity of the phosphoric acid contained in the precipitates which have



formed. This may be done by the simple method which has been described before. The precipitate is ignited, after which, if it consists of phosphoric acid and baryta, it is first treated by sulphuric acid, then by water. If protoxyde of lead or lime has been employed to precipitate the phosphoric acid, weak alcohol is used instead of water. The quantity of sulphate thus obtained is afterwards determined, from which that of the baryta, of the protoxyde of lead, or of the lime, is calculated, and afterwards that of the phosphoric acid which was combined with these bases in the precipitate.

The quantitative determination of phosphoric acid by means of the solutions of chloride of barium and chloride of calcium, or of a salt of lead, becomes still more uncertain when the combination contains sulphuric acid besides. It is true that the latter may be easily removed by means of a solution of a salt of baryta, as I have already said, for sulphate of baryta alone can, thus be precipitated from an acid liquor. Yet, for the reasons which I have developed before, the phosphoric acid contained in the filtered liquor cannot be precipitated completely in the state of phosphate of baryta by supersaturating the liquor with ammonia. The quantitative determination of sulphuric and of phosphoric acids, when simultaneously present, can hardly ever be attended with success, and at any rate, only when these acids are combined with bases capable of being precipitated by sulphuretted hydrogen in the state of metallic sulphurets. In such cases the combination is dissolved in nitric acid, and, after diluting the solution, the metallic oxydes are precipitated therefrom by sulphuretted hydrogen, the liquid is filtered, heated in order to expel all the free sulphuretted hydrogen which it may contain, and a solution of nitrate of baryta is afterwards added. The precipitated sulphate of baryta is weighed, and from its weight the quantity of the sulphuric acid is calculated. The quantity of this acid may be greater than that which is actually contained in the solution, because the action of sulphuretted hydrogen upon dilute nitric acid, produces sometimes a little sulphuric acid.

\* The liquor filtered from the sulphate of baryta produced is then evaporated with care to dryness, the dry residuum is then ignited and weighed. The quantity of the baryta contained in the residuum is determined in order to estimate that of the phosphoric acid from the loss. To effect this the ignited mass is decomposed by sulphuric acid, and, from the weight of the sulphate of baryta which is thus formed, the quantity of the baryta which it contains is calculated.

In adding nitrate of baryta, great care should be taken to pour only a little more of it than is strictly necessary to precipitate the sulphuric acid. The excess employed varies with the quantity of the phosphoric acid. If too much nitrate of baryta has been employed, the result will subsequently be that when the excess of this salt comes to be decomposed during the ignition, carbonate of baryta is produced from the action of the air, which will, of course, completely vitiate the analysis.

In the analysis of phosphates the bases may often be precipitated by an excess of solution of pure potash, by which means they may be separated from phosphoric acid. But this method yields results which are quite as inaccurate as those obtained by separating arsenic acid from metallic oxydes, by means of pure potash (page 341). However large may be the excess of potash employed, the metallic oxydes precipitated by this reagent can very seldom be obtained free from phosphoric acid.

It is easily seen from that which has been said, that the method which consists in precipitating phosphoric acid by solution of a salt of lead, previous to the determination of the bases, cannot be applied here any more than for arsenic acid (page 344).<sup>1</sup>

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<sup>1</sup> M. Erdman proposed some years ago to estimate the constituents of perphosphate of iron, by precipitating with ammonia, mixing it with a sufficient quantity of carbonate of soda, and igniting the mixture in a platinum crucible. The soda becomes thus converted into phosphate of soda, which he separates, by filtering, from the insoluble peroxyde of iron. If the perphosphate of iron was mixed with phosphate of alumina, the alumina would be dissolved by the alkaline salt; by saturating the excess of carbonate and adding ammonia to the solution, it is precipitated in the

DETERMINATION OF PHOSPHOROUS AND HYPOPHOSPHOROUS  
ACIDS IN THEIR COMPOUNDS.

When the quantity of phosphorous and of hypophosphorous acids in the combinations which these acids form with bases has to be determined, these combinations are first converted into phosphates, which are then analysed by the methods which have been mentioned before. In order to transform phosphites and hypophosphites into phosphates, a certain quantity of the combination under examination is first weighed, it is put in a shallow platinum capsula, nitric acid is poured upon it, and the whole is evaporated to dryness; the residuum is then ignited with care. Thus treated, the neutral phosphites yield neutral phosphates; but the neutral hypophosphites are converted into acid phosphates.

The quantitative determination of phosphorous acid would be more simple, if it was only necessary to dissolve its combinations in water, or in acids, and only to determine the quantity of the bases in the solution. But all the phosphites contain water which cannot be expelled by a gentle heat, because it is constitutional water, that is, water necessary to the existence of these salts; and hence, the quantity indicates collectively phosphorous acid and water. It is therefore necessary to weigh a certain quantity of the phosphite, and to transform it into phosphate, which is afterwards weighed, and in which the quantity of base which it contains is determined. The quantity of phosphoric acid produced by the oxydisation being thus arrived at, it is easy to calculate from it that of the phosphorous acid, which has been thus converted into a higher degree of oxydisation. The quantity of the base, and of the acid in the phosphite being thus determined, the loss indicates how much water was contained in this salt.

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state of basic phosphate of alumina; the liquor is then acidified by acetic acid, and, by means of acetate of lead, the phosphoric acid contained in the solution is finally precipitated.—Ed.

The phosphites of alkalies are soluble in water, but the combinations of phosphorous acid with the other bases are only soluble in acids.

The hypophosphites are all soluble in water, wherefore the bases can be precipitated from their solutions and quantitatively determined by the ordinary methods. When hypophosphorous acid is combined with metallic oxydes, the latter may also be precipitated by alkalies, when capable of being thus precipitated. The earthy hypophosphites are precipitated by the reagents which have been spoken of before in the chapters which treat of these salts.

When the operator wishes to determine in hypophosphites the quantity of the acid and of the water, of which water often the whole, but frequently also a part only, is necessary to the existence of the salt, a certain portion of the latter is weighed, and nitric acid being poured upon it, the whole is evaporated to dryness; the dry mass is afterwards ignited. The hypophosphorous acid is thus converted into phosphoric acid. The combination is then weighed, and the quantity of base which it contains is determined, by which that of the phosphoric acid becomes known, and from which that of the hypophosphorous acid is calculated. The loss indicates the quantity of the water. This mode of operation presents, however, a peculiar difficulty. The hypophosphites, when treated by nitric acid, are transformed into acid phosphates, which after ignition are insoluble in muriatic acid, and, therefore, are difficult to decompose. In order to render them soluble, they are treated by sulphuric acid in the manner described before, or else, before treating the hypophosphites by nitric acid, a weighed quantity of base is added.

## DETERMINATION OF THE QUANTITIES OF THE ACIDS OF PHOSPHORUS WHEN SOME OF THEM EXIST SIMULTANEOUSLY.

When a liquor contains both phosphoric and phosphorous acids, or phosphoric and hypophosphorous acids, and their respective quantities have to be determined, it may be done in a very accurate manner by the following method:—The liquor is gradually poured, and by small portions at a time, into a fully saturated solution of perchloride of mercury. The precaution (pouring small portions at a time) is necessary, because, if too large a quantity of the acid liquor under examination was at once poured into the solution of perchloride of mercury, or *vice versa*, a large quantity of the latter into the former, a separation of mercury in the metallic state might take place, which accident must be absolutely avoided. Subchloride of mercury soon precipitates, with a lustre like that of mother-of-pearl, and which gradually increases. The whole is left to digest for several days at a very gentle heat, because the last portions of the subchloride of mercury subside very slowly, and only by a prolonged digestion. The precipitate is collected upon a weighed filter, dried at an exceedingly moderate heat, until it ceases to lose weight, and it is then finally weighed. From the quantity obtained, that of the phosphorous, or of the hypophosphorous acid are calculated, both these acids having been converted into phosphoric acid.

Another portion of the liquor under examination is mixed with nitric acid and with a weighed quantity of protoxyde of lead, in order to determine, by the method indicated before (page 426), the quantity of the phosphoric acid, part of which existed already in the liquor, whilst the other portion arises from the decomposition of the nitric acid by the phosphorous or hypophosphorous acid. The first experiment having indicated how much phosphoric acid was produced by the phosphorous or hypophosphorous acid, the operator, by deducting that quantity from the whole of the phosphoric acid obtained, may thus learn how much of the acid existed in the compound.

It is easy by this method to analyse the acid which is produced by the deliquescence of phosphorus in the air. It never happens that a liquor contains simultaneously the three acids of phosphorus, and, consequently, the quantity of each of these acids has never to be determined in a same liquor.

When combinations of phosphates, of phosphites, and hypophosphites, have to be analysed, they are dissolved in water; or if insoluble therein, they are dissolved in muriatic acid; the liquor is acidified, in the first case, with muriatic acid, and the operator then proceeds as we have just said.

## CHAPTER XLIV.

## SILICIUM.

## DETERMINATION OF SILICIC ACID.

THE quantity of silicic acid contained in an alkaline, or in an acid liquor, cannot be determined in any other manner than by evaporating the solution to perfect dryness. If the liquor is alkaline, it must first be acidified by adding muriatic acid thereto.

\* During the evaporation, the silicic acid is gradually separated under the form of a jelly. When the acid liquor has been reduced to a certain volume, and is suffered to cool, it is found, after cooling, in the state of a firm jelly; but in that state, the silicic acid is not as yet quite insoluble in water; it is only after having completely dried this jelly that it becomes insoluble. The dry mass is then treated by water, the silicic acid is separated by filtering, it is washed and ignited in a platinum crucible. Silicic acid must be perfectly dry before being submitted to ignition, otherwise it may be projected as dust, and a loss thus easily be sustained. Immediately after this, the crucible must be closed with a tight cover, and, when cold, the whole is weighed. If the silicic acid were suffered to cool without covering the crucible, it would attract moisture with still more rapidity than other pulverulent substances.

Silicic acid forms with other oxydes, compounds, some of which are easily decomposed by stronger acids, whilst others resist the action of the most powerful acids. The process to be followed for the analysis of silicious compounds which can be

easily decomposed by acids, is quite different from that which must be resorted to for such of those compounds as are not attacked by acids. I have given, in the first volume, a list of the native silicious compounds which are decomposed by, and which resist the action of acids.—(Vol. I., page 287.)

**SEPARATION AND DETERMINATION OF SILICIC ACID, IN COMPOUNDS WHICH ARE CAPABLE OF BEING DECOMPOSED BY ACIDS.**

The analysis of the silicates which can be decomposed by acids is much more simple than that of the other silicates. Muriatic acid (somewhat concentrated) is generally used in preference to decompose these combinations. It is only in a small number of cases that nitric acid, or even sulphuric acid, are employed instead. Although most of the combinations of silicic acid can be decomposed by sulphuric acid, when they are digested in a state of fine powder with this acid, yet it is seldom resorted to, because its employment has many drawbacks which will be mentioned farther on.

The silicate to be analysed is first reduced into fine powder without addition of water, in order to be able to weigh exactly a certain quantity of it, and the powder thus weighed is put in a platinum crucible, which must be very moderately heated. The operator must take great care that the temperature does not exceed that of boiling water, because many silicates contain water or other volatile substances, a portion of which would then be disengaged. Moreover, a great many silicates can no longer be decomposed by acids after their volatile constituent has been expelled by a strong heat or by ignition.

The weighed portion of the silicate is put in a glass, which is closed by a glass-plate fitting well, and muriatic acid is poured upon it. The glass must be of a kind capable of resisting the action of acids. The various combinations of silicic acid are differently decomposed. Some of them are decomposed almost instantaneously; the silicic acid separates in the form of a jelly and when too large a proportion of silicic acid has not been



employed, it absorbs all the acid, and the result is a swelled mass of a gelatinous appearance. Other silicates, also in powder, are likewise easily decomposed by muriatic acid, but the silicic acid separates in the form of a light flocculent powder, and does not form a jelly. Others again are difficultly decomposed by muriatic acid, and it is necessary, after having reduced them into very fine powder, to digest them for a long time in that acid, with the help of heat, in order to decompose them.

The decomposed and gelatinous combination is treated by a little water; the silicic acid separates under the form of light flocks. Before collecting it upon a filter, the operator must examine whether the combination has been completely decomposed by the acid. This is done in a very simple manner, and which is the same for all the silicates which can be decomposed by acids:—A glass rod is rubbed against the bottom and sides of the glass; if this produces a gritty noise similar to that produced by rubbing fine sand between two pieces of glass, it is owing to the presence of a certain quantity of undecomposed powder. In this case, the operator will notice that, under the flocks of silicic acid, there is a deposit of a heavier powder. The liquor must then be decanted with the silicic acid in suspension, and the undecomposed portion is then treated by a fresh quantity of muriatic acid. When, however, the combination under examination is one which is easily decomposable by acids, this powder is generally produced by some foreign substances, which were enclosed in the silicate, and upon which the acid employed has no decomposing action. In such a case, the residuum must be levigated in order to separate the silicic acid, which is lighter, and the undecomposed powder remains at the bottom of the glass. This operation is very easily performed, and does not require much practice; the foreign substance is dried in the glass, its weight is determined, and it is deducted from that of the combination experimented upon.

The silicic acid is collected upon a filter, the water passes through the filter slowly, but the washing need not last long, because in the case under present consideration, the silicic acid

is easily washed. It is necessary after having poured a sufficient quantity of water upon the decomposed gelatinous combination, and stirred the whole, to leave it at rest for a long time (about twelve hours) in order that the silicic acid may settle completely. The clear supernatant liquor filters much more rapidly than when turbid. After washing the silicic acid it is dried and ignited in a counterpoised platinum crucible. Immediately after the ignition, the crucible is shut with a close cover, and the silicic acid is weighed. The whole of the silicic acid which existed in the compound submitted to analysis cannot, however, be obtained in this manner; a very small quantity of the acid, but which ordinarily does not exceed one per cent., remains in solution in the acid liquor, from which it is precipitated along with the other substances which it still contains.

It is customary also after the decomposition of the compound, by muriatic acid, to evaporate the whole to dryness, and to volatilise thus all the excess of acid, so that, upon treating the dry mass by water, the whole of the silicic acid remains undissolved. This method in most cases does not answer the purpose, for when employed, a large proportion of silicic acid remains, yet a small quantity of it dissolves notwithstanding, especially when the dry mass is not immediately treated by water, which is generally the case, since the operator is often obliged to treat it previously by muriatic acid, as I shall have occasion to remark farther on. Since then, the whole of the silicic acid does not remain insoluble, small portions of which have to be subsequently separated in the course of the analysis, this operation of drying is useless, and should, therefore, be dispensed with, not only because it presents difficulties, but principally because it may be a source of loss. Moreover, there are certain volatile principles which might be completely expelled by evaporating the acid liquor to dryness. It has happened to many chemists to overlook in the analysis of silicates the presence of certain substances which had volatilised during the drying. Wherefore, the combinations which are easily decomposed by muriatic acid should be digested only in the

cold, and heat should be applied only for the silicates which are more difficult to decompose.

Most of the oxydes which are met with in combination with silicic acid, being very soluble in muriatic acid, are found in the liquor which has been filtered from the silicic acid. If the combination contains *protoxyde of lead* or *oxyde of silver*, it must be treated by nitric acid, and not by muriatic acid, because a great portion of the chloride of lead, and the whole of the chloride of silver would remain mixed with the undissolved silicic acid. The combinations which form a jelly by being decomposed by acids never contain these two oxydes, which are frequently met with only in artificial combinations, for example, in certain enamels which may be easily and completely decomposed by digestion in hot nitric acid, after having previously reduced them into fine powder.

The other substances contained in the liquor filtered from the silicic acid are separated by the methods which have been fully described before. The method most generally employed for the analysis of the native silicates is the following:—After having separated the silicic acid, the acid liquor is neutralised by ammonia, a slight excess of which should be added. This alkali completely precipitates the alumina and peroxyde of iron; small quantities of magnesia and of protoxyde of manganese are precipitated at the same time. These substances are separated from each other by the methods which have been indicated (page 76.) The liquor is filtered, the lime is precipitated therefrom by oxalate of ammonia, and, if it contains neither magnesia nor protoxyde of manganese, the fixed alkali which it may contain is determined by evaporating to dryness the liquor filtered from the oxalate of lime, and heating the dry mass for a long time to incipient redness. The chloride and oxalate of ammonia are volatilised, whilst the alkali remains in the state of metallic chloride. If magnesia exists with the alkali, the determination of these two bases presents some difficulties, and

should be effected as we said (page 42). But if it contains no alkali, after having separated the lime, the magnesia is determined by treatment with carbonate of potash, or, what is better still, and provided muriatic acid has been employed to decompose it, the whole is evaporated to dryness and the magnesia is obtained by repeatedly igniting it with carbonate of ammonia, (page 44).

I should remark also that most of the substances which are separated during the course of this analysis contain very small quantities of silicic acid, which, in all cases of extreme accuracy, should be determined. This is done by igniting and weighing each substance separately, and dissolving it in muriatic acid, which has no action upon the slight quantity of silicic acid. The latter is collected on a filter, washed, ignited, and its weight is then determined and added to that of the silicic acid obtained at the beginning of the analysis. In thus dissolving three or four substances small quantities of silicic acid are obtained which, however, when collected together, amount barely to one hundredth part of the substance submitted to analysis, as I said before, and which small quantities are neglected in such analyses which need not be very accurate. It is in redissolving magnesia that the greatest proportion of silicic acid is obtained, when this base comes subsequently to be precipitated by carbonate of potash, from which latter substance it is generally derived. If carbonate of potash has not been employed to precipitate the magnesia, no residuum of silicic acid, or, at least, a very trifling one, is obtained. Much less silicic acid still is found by redissolving the alumina and peroxyde of iron, and the carbonate of lime obtained always redissolves without residuum.

SEPARATION AND DETERMINATION OF SILICIC ACID, IN COMPOUNDS WHICH CANNOT BE DECOMPOSED BY ACIDS.

*Decomposition of such combinations by Carbonate of Alkali.*

The analysis of the silicates which cannot be decomposed by acids is more difficult. A few of them, such as garnet,

idocrase, and epidote, may be completely decomposed, according to Kobell, by muriatic acid ;<sup>1</sup> when, after having ignited or fused and then reduced them to powder, they are treated by that acid, in which case they form a jelly. Most of them, however, are decomposed after having reduced them into very

<sup>1</sup> Garnet, idocrase, and epidote, are minerals, including several varieties, which consist of the same elements.

The precious garnet of Bohemia, analysed by Vauquelin, gave,—

Silica . . . . .	36·00
Alumina . . . . .	22·00
Protoxyde of Iron . . . . .	36·80
Lime . . . . .	3·00
	<hr/>
	97·80

The green garnet, or grossularite of Norway and of Siberia :

	NORWAY.
Silica . . . . .	38·80
Alumina . . . . .	20·40
Lime . . . . .	32·00
Protoxyde of Iron . . . . .	8·35
	<hr/>
	99·55—Richardson.

The black garnet (Melanite) :

Silica . . . . .	35·50
Alumina . . . . .	6·00
Lime . . . . .	32·50
Protoxyde of Iron . . . . .	24·25
Protoxyde of Manganese . . . . .	0·40
	<hr/>
	98·65—Klaproth.

Idocrase (pyramidal garnet), from Vesuvius :

Silica . . . . .	37·359
Alumina . . . . .	23·520
Lime . . . . .	29·681
Protoxyde of Iron . . . . .	3·992
Magnesia, and Protoxyde of Manganese . . . . .	5·208
	<hr/>
	99·760—Magnus.

Epidote (crystallised) :

Silica . . . . .	37·0
Alumina . . . . .	21·0
Lime . . . . .	15·0
Oxyde of Iron . . . . .	24·0
Oxyde of Manganese . . . . .	1·5
	<hr/>
	98·5—Vauquelin.

fine powder, and fused then with carbonate of potash ; the silicic acid combines then with the potash to form silicate of potash, and the bases which were combined with it, are set at liberty. After fusion with carbonate of potash, the mass may be completely decomposed by acids.

Many precautions must, however, be observed in such an analysis. The operator must first take great care to pulverise the silicate as finely as possible, before fusing it with carbonate of potash, for otherwise its decomposition would not, in many cases, be effected in a complete manner. In order to pulverise the substance to be analysed to the requisite degree of fineness, it is first broken into coarse grains, which operation may be performed in a steel mortar, but the same result may be obtained as well by wrapping the substance in paper, and crushing it with a hammer upon a hard stone or a plate of iron, so that the steel mortar may thus be dispensed with. The coarse powder is afterwards trituated in a mortar of agate or better still, upon a slab of agate with water. When the operator thinks that a great portion of the substance has attained a sufficient degree of division, the whole is poured out in a glass, water is added, and the mass is stirred with a glass rod, and left at rest for a few moments, in order that the coarsest powder may settle. The fine particles remain in suspension in the water, which is to be poured in another glass. The coarse powder is again trituated in the mortar, and the same experiment as before is repeated. The fine particles suspended in the water are allowed to settle completely, and it is separated from the liquid by decantation, and dried. The decomposed water contains still a small portion of the pulverised compound which renders it opaline and which can be obtained by evaporating it to dryness, for it cannot be separated by filtering.

In most cases when it is not necessary to reduce the silicate to an extreme degree of division, the operator only triturates it with water in an agate mortar, and then pours a large quantity of water in the mortar; the whole is then stirred, and

transferred to another vessel by means of a glass syphon ; the coarsest parts remain in the mortar, and are triturated again.

When the triturated substance is less hard than agate, it may be assumed that nothing has been abraded from the mortar ; but if the substance be harder, which, however, is rarely the case, this effect must, of necessity, take place. This is a very troublesome circumstance, because it is difficult to ascertain how much the mortar has lost by abrasion. It has been proposed to weigh the mortar accurately, and to ascribe the augmentation of weight of the powder after trituration to the abrasion of the mortar, but such a determination is very difficult, and can but seldom be accurately ascertained ; it is almost preferable to triturate the coarse powder in a small crucible, previously counterpoised, in scales capable of indicating larger weights with precision ; if then, after the operation, the mortar weighs a little less, the difference must be ascribed to loss from abrasion. As agate consists almost entirely of pure silicic acid, the quantity which has been abraded is afterwards deducted from that of the silicic acid obtained, and from that of the silicate submitted to analysis. But this method is also very difficult. The small number of silicates which can be decomposed by carbonate of alkali, and which are harder than steel, might, however, be pulverised in a steel mortar, as will be said farther on.

The quantity of fine powder which it is intended to submit to analytical research is put in a small counterpoised platinum crucible, in which it is warmed, and then slightly ignited, until it ceases to loose weight, after which its weight is noted. If the substance contains protoxyde of iron or another oxyde the composition of which is altered by ignition, the powder must not be exposed to a red heat, but merely dried before weighing it. When it is dry it is carefully shaken into a larger platinum crucible. As it often happens that a very slight portion remains in the smaller crucible, the operator must take care to weigh it again, by which means the operator may ascertain that a few milligrammes of the powder have remained attached thereto,

and which must be deducted from the quantity of that on which the analysis will be performed.<sup>1</sup>

The powder is very carefully mixed in the large platinum crucible, with three or four times its weight of pure carbonate of potash, which should be previously pulverised in a warm mortar. The mixture is effected by means of a small glass rod, and must be continued until the mixture has become quite homogeneous, yet it should not be continued too long, otherwise the carbonate of potash would absorb moisture; that which adheres to the glass rod is carefully detached with a dry feather.

In most cases carbonate of soda, previously deprived of its water, can be advantageously used instead of carbonate of potash. This salt does not absorb moisture whilst being mixed with the pulverised silicate, and as it contains no silicic acid, the operator is sure that it will not increase the quantity of that substance, which certainly is not the case when carbonate of potash is used, added to which, a less quantity of carbonate of soda answers the purpose.

When the mixing is finished, the crucible is covered up and put in a wind furnace amongst charcoal. A moderate heat is at first given, but it is soon increased, so that the crucible remains exposed to a red heat for half an hour or an hour. As

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<sup>1</sup> At a red heat the following oxydes absorb oxygen, and pass to a higher degree of oxydisation.

Protoxyde of Barium	becomes	Binoxide of Barium.
Protoxyde of Potassium	—	Peroxyde of Potassium,
Protoxyde of Sodium	—	Peroxyde of Sodium.
Protoxyde of Tin	—	Peroxyde of Tin.
Protoxyde of Manganese	—	Sesquioxide of Manganese.
Protoxyde of Iron	—	Sesquioxide of Iron.
Protoxyde of Molybdenum	—	Molybdic Acid.
Deutoxyde of Molybdenum	—	Molybdic Acid.
Oxyde of Tungsten	—	Tungstic Acid.
Oxyde of Titanium	—	Titanic Acid.
Suboxyde of Copper	—	Protoxyde of Copper.
Protoxyde of Lead	—	Minium or Red Lead.
Suboxyde of Mercury	—	Protoxyde of Mercury.—Ed.



a platinum crucible is often injured when placed between burning charcoal and becomes incrustated here and there, but principally about the cover, with a fused mass produced by the silicic acid and oxydes contained in the ashes of the charcoal, and which it is difficult to remove, the platinum crucible should be put within a hessian crucible of a cylindrical form, and which is likewise covered up. This precaution prevents, besides, the platinum crucible from being upset when the charcoal is burnt out.

According as the substance submitted to analysis contains more or less silicic acid, and the quantity of carbonate of potash added being about uniform, the mass in the crucible is either completely fused or only agglomerated. If the compound contains any manganese, the fused mass has a greenish-blue or a blue tinge, according as the metal contained in it is more or less abundant. The crucible is turned upside down over a glass, and the operator endeavours to detach the fused mass and to make it fall therein, which is done by slightly compressing and bending the crucible. When the mass is only agglomerated, it may thus easily be detached, and it then generally falls in one lump; but when the mass is fused, it is more difficult to remove it from the crucible by bending it, and whatever efforts are made, a certain quantity remains attached thereto. This remaining portion is softened by water, and as much of it as possible is conveyed to the glass; but in order to remove the last particles adhering to the crucible, dilute muriatic acid is poured into it, by which they are readily dissolved. It is likewise more easy to remove the larger portions of the fused mass by muriatic acid, than by softening them with water, but the operator must then use great caution, for if a great quantity of acid be employed at a time, the disengagement of carbonic acid which takes place produces a strong effervescence, from which a loss may arise.

If the calcined mass contains manganese, cerium, or chromium, water only must be used to soften it in the crucible, because the higher degrees of oxydisation of these metals decompose muriatic

acid, from which they evolve chlorine, which would attack the crucible; this effect may even be produced, if the combination contain only one or two per cent. of protoxyde of manganese.

The fused mass being now collected in the glass, the supernatant liquor is acidified by muriatic acid; but this must be done with caution, and the acid should only be poured by small portions at a time, in order to avoid so strong an effervescence. The glass should also be covered with a concave piece of glass. When the effervescence, which is always strong, has ceased, the glass is left in a warm place, and after having thus left it to digest for a sufficient time, the whole will have decomposed. A great portion of the silicic acid remains under the form of light flocks, and another portion dissolves in the liquor. It often happens, also, that the whole of the silicic acid dissolves pending the treatment with muriatic acid, which is especially the case when a large quantity of carbonate of potash has been employed, and much water has been poured upon the fused mass to soften it, but more especially still when the combination contains only a small quantity of silicic acid. It is now that the operator may see whether the substance submitted to analysis has been completely decomposed by ignition with the carbonate of potash; this is ascertained by rubbing a glass rod against the sides and the bottom of the glass. If any powder has escaped decomposition, it is immediately discovered by the gritty noise which is then heard.

The acid liquor is evaporated to dryness, along with the silicic acid which has separated. This evaporation may be performed in a platinum capsula, or else in one of porcelain. When the compound contains manganese, cerium, or chromium, a porcelain capsula must always be employed. The evaporation is effected upon the sand-bath, at a gentle heat, which, especially towards the end must not be too strong. The capsula should be covered with filtering paper to prevent any dust from falling in the liquor; but the paper should be changed very often, because the vapours of muriatic acid, which are evolved soon corrode it. When the liquor has been reduced by evaporation to syrupy

consistence an extremely gentle heat only must be used, for, if a stronger heat were applied, the silicic acid which has separated under the form of a jelly might cause a projection, which would render the analysis inaccurate. If, however, the operator wishes to accelerate the evaporation by means of a stronger heat, he must take care to stir the mass constantly with a glass rod. The heat is withdrawn only when the whole mass has become perfectly dry. When the evaporation is performed on the water-bath, no projection need be apprehended, even though the mass be gelatinous. But towards the end, that is, just before it has completely dried, a stronger heat than can be produced by the water-bath may be applied.

After cooling, the dry mass is uniformly drenched with concentrated muriatic acid, and left in contact with the acid for half an hour. Water is then poured upon it, all the portions of the substance which have combined with the muriatic acid are dissolved, whilst the silicic acid remains. The latter is collected on a filter, washed, and thoroughly dried, ignited, and weighed.

The muriatic acid solution, filtered from the silicic acid, is treated as we have said, page 455, when treating of the silicious compounds, which are decomposed by acids.

The various substances which are obtained separately in these analyses, are likewise accompanied by silicic acid, the weight of which must be determined in all cases of rigorously accurate analysis.

If the substance contained any protoxyde of iron, it will have been completely transformed by the drying of the muriatic acid solution into peroxyde of iron, which renders it useless to add nitric acid, which, for other reasons, should be avoided.

The dry mass is drenched with muriatic acid, because, during the operation, and especially towards the end, when the mass begins to dry, and the heat is augmented, several substances loose a portion of their acid, and thus become partially insoluble in water. The magnesia, alumina, and peroxyde of iron, are the substances which mostly become insoluble in water by strong ignition, and, in order to render them soluble in water, they must be

previously moistened with muriatic acid ; the solution, however, does not take place in a complete manner, when the operator only pours on the dry mass very dilute muriatic acid. In that case, if a large quantity of peroxyde of iron is present, the silicic acid will always have a reddish tinge, owing to the presence of this oxyde, which is not the case when, before adding water to the dry mass, it has been treated by muriatic acid.

DETERMINATION OF THE FIXED ALKALIES IN SILICIOUS  
COMPOUNDS.

When a silicious combination has been decomposed by fusion with carbonate of potash, almost all its constituents may be quantitatively determined in the usual manner ; but another process must be adopted for the quantitative determination of the fixed alkalies when they are contained in a silicious compound. When this is the case, if the operator possesses a sufficient quantity of the substance, a portion thereof is ordinarily decomposed by carbonate of potash, for the purpose of determining the quantity of the silicic acid, and of most of the other constituents, and another portion is devoted to the determination of the fixed alkalies. These operations are, however, attended with difficulties which render most of the methods hitherto proposed inadequate to the rigorous determination of the alkalies, the quantity obtained being always less considerable than that really existing in the compounds.

Several methods may be employed for the quantitative determination of the alkalies in silicious compounds which cannot be decomposed by acids, but I shall only take into consideration those which can really yield accurate results when performed with the requisite care. To effect this the substance may be decomposed either by carbonate of baryta, or by fluor spar, or by hydrofluoric acid.

DECOMPOSITION OF SILICIOUS COMPOUNDS BY CARBONATE OF  
BARYTA.

When the operator wishes to decompose the silicious compound by carbonate of baryta, it must be first reduced into extremely fine powder ; the powder must be finer than for the decomposition by carbonate of potash. The quantity of powder which is selected for analysis is weighed, and mixed most intimately in a platinum crucible with five or six times its weight of very pure carbonate of baryta, which must not have been obtained by precipitation from a solution of a baryta-salt by means of a carbonate of fixed alkali, because it might possibly retain a small proportion of the latter. Carbonate of ammonia is the only agent which can be employed to precipitate it for the use in question.

The mixture of the two powders must be most exactly performed, because on this the complete decomposition of the substance depends. The compound is much more difficultly decomposed by carbonate of baryta than by carbonate of potash, because the latter, on fusing, comes in contact with all the parts of the powder, even when the mixing has not been intimate, and, therefore, fusion with this salt always decomposes the compound completely. Unless a white heat be employed, carbonate of baryta does not fuse, and, with silicious substances, it only becomes agglomerated, and, moreover, this effect takes place only when each molecule of the compound is wrapped up, as it were, in carbonate of baryta. Wherefore the operator must take the greatest pains to mix the carbonate of baryta and the compound most intimately, which cannot be done in less than, at least, half an hour.

The mixing being finished, the platinum crucible is exposed to an intense heat, which must be stronger than when carbonate of potash is employed ; the more intense the heat, the more complete the decomposition is.<sup>1</sup> After the ignited mass has

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<sup>1</sup> The heat applied is so intense, that some precautions must be taken. The platinum crucible containing the mixture should be exposed first to the heat of an

quite cooled, it is treated exactly in the same manner as if it had been fused with carbonate of potash. The agglomerated mass is shaken into a glass, and digested with muriatic acid, which, however, should be diluted with a pretty large quantity of water; neither must too large an excess of it be employed, because the chloride of barium formed is difficultly soluble in muriatic acid, especially when not very dilute.

When the decomposition of the mass, by the acid, is finished the operator must carefully examine whether any portion of the powder is still undecomposed, which is especially the case when the mixing of the substance with the carbonate of baryta has not been very intimate. In such a case, it would almost be better to begin the analysis *de novo*, provided the operator has yet enough of the substance; if, however, he cannot or will not do so, he must endeavour to separate the light, flocculent silicic acid from the undecomposed heavy powder by levigation; the weight of the portion which has thus escaped decomposition is then deducted from the quantity of the compound experimented upon.

The quantity of the silicic acid set at liberty is larger when carbonate of baryta than when carbonate of potash has been

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argand spirit-lamp, and when the mass begins to agglutinate, the crucible should be closed, and its cover tied over with platinum wire, and the whole is placed in a hessian crucible, closed up also; the whole is then placed upon an inverted crucible, and submitted to the action of the blast, or wind-furnace, beginning first gradually with a red heat, piling more coke, so as to fill up the furnace, and increasing the heat to the highest possible pitch, until the hessian crucible begins to soften,—fresh coke being added as it consumes. When the crucible begins to soften, as we have said, the operation must be stopped, because the hessian crucible would fuse, and damage the platinum one inside. It is absolutely necessary to the success of the operation, that the hessian crucible should be closed as well as possible, which is best done by luting the cover with fire-clay, and the blast must not be too powerful, neither must the fusion be continued more than about a quarter of an hour. The crucible, on being withdrawn from the furnace, should be placed into sand, in order that it may cool slowly. The hessian crucible and its cover having fused together cannot be separated, except by breaking, and the platinum crucible is found inside in a perfect state. If the operation has been carefully performed, the mass in the platinum crucible is perfectly fused, and is covered with shining acicular crystals. It may be easily detached from the crucible, and on treating it with muriatic acid, scarcely any effervescence is produced, the heat having expelled most of the carbonic acid of the carbonate of baryta.—ED.

employed, yet a considerable quantity always remains dissolved in the acid liquor, and which may be separated as has been said (page 463). The liquor is evaporated to perfect dryness, and the dry mass is afterwards moistened with muriatic acid, perfectly free from sulphuric acid, and left at rest for half an hour, in order to give the acid time to act. Water is then added, the silicic acid remains undissolved. The analyst must never omit to determine its weight, even though the quantity of the silicic acid contained in the substance under examination may already have been determined, in a previous operation, by fusion with carbonate of potash. If the weights of the two quantities of the silicic acid obtained agree, the operator may rest assured that the substance has been as completely decomposed by the carbonate of baryta as by the carbonate of potash.

Sulphuric acid is then poured in the muriatic acid liquor filtered from the silicic acid; the baryta is thus precipitated in the state of sulphate of baryta. A large excess of sulphuric acid must, however, be carefully avoided, because the less considerable that excess is, the more easily is the quantity of the alkali determined. The bulky mass of sulphate of baryta obtained is washed, and when the compound contains much lime, the washing must be continued for a long time. If the quantity of this latter substance be very considerable, the sulphate of baryta is not washed until it no longer contains any sulphate of lime, but only until all the sulphate of alkali has been washed away.

Ammonia is then ordinarily poured in the liquor, by which means the peroxyde of iron and the alumina is precipitated. It is advisable to determine the quantities of these two substances separately, and to compare them with those which have been obtained in the other analysis in which the substance had been decomposed by carbonate of potash. The liquor is filtered, and by means of oxalate of ammonia the sulphate of lime, if any be held in solution, is precipitated. If, now, the liquor contains no magnesia, nor protoxyde of manganese, nor any other substance which cannot be precipitated all or only imperfectly

by ammonia, the liquor thus filtered from the precipitate produced by oxalate of ammonia contains no other fixed constituents than alkalies, which are then in the state of sulphates. This liquor is evaporated to dryness, the dry residuum is ignited, in order to volatilise the ammoniacal salts, and the residuum consists of an acid sulphate of alkali.

In igniting the dry mass, the operator must be extremely careful, because it is during this part of the process that the greatest loss of alkali may take place. In effect, besides the sulphate of fixed alkali, the dry mass contains sulphate of ammonia, muriate of ammonia, and oxalate of ammonia, when this reagent has been employed to precipitate the lime. The muriate of ammonia is easily volatilised at a red heat without fusing; the small quantity of oxalate of ammonia is converted into carbonate of ammonia, which volatilises also without loss; but when heated, the sulphate of ammonia fuses and boils, and the result is a pretty strong projection, which may cause the loss of a certain quantity of sulphate of fixed alkali. The less is the excess of sulphuric acid employed to precipitate the baryta, the easier it is to expel the salts of ammonia, because there is not much sulphate of ammonia present. In order to ignite the dry mass, the best is to put it first into the large platinum capsula which was first used to evaporate the liquor, because the chances of loss by projection are thereby much lessened. When almost all the volatile salts have evaporated, the residuum is washed, by means of a little water, into a small counterpoised platinum capsula or crucible, evaporated to dryness, and ignited. As this residuum is altogether an acid sulphate of alkali, some carbonate of ammonia must be added during the ignition (page 2), by which means a neutral sulphate of alkali is obtained, the weight of which is determined, and from which the quantity of the alkali is calculated.

When magnesia exists in conjunction with the alkali in the substance submitted to analysis, the determination is more difficult still, and is attended with considerable loss. In such a case, the liquor which was filtered from the oxalate of lime, and



which now contains no other fixed principles than magnesia and alkali, and the solution of a very small quantity of magnesia, which was precipitated by ammonia previously, is added thereto; it is then evaporated to dryness, the collective weight of the sulphate of alkali and of magnesia is determined, and they are separated from each other by a solution of acetate of baryta in the manner indicated before (page 42).

\* The best method of determining the small quantity of magnesia which, in the analysis of silicious compounds by ammonia, has been precipitated along with the alumina and peroxyde of iron, consists in reducing it into phosphate of magnesia. This is done by pouring in the liquor, filtered from the persuccinate of iron, a solution of phosphate of soda with the addition of ammonia. It is not advisable to mix this liquor with that which has been filtered from the oxalate of lime.

As it is very difficult to determine with rigorous accuracy the quantity of the sulphate of fixed alkali from that of the sulphate of ammonia which accompanies it, another process must be adopted. Carbonate of ammonia is added to the muriatic acid liquor which was filtered from the silicic acid. This reagent precipitates the carbonate of baryta and the carbonates of alumina, of peroxyde of iron, &c. The liquor is filtered, evaporated to dryness, and the dry residuum is ignited, by which means the alkali is obtained in the state of metallic chloride. This method, however, does not yield an accurate result. Carbonate of baryta not being quite insoluble, and the quantity of this salt being somewhat considerable, a certain portion thereof always dissolves during the washing. The carbonate of baryta thus dissolved, being in presence of muriate of ammonia in the liquor, is converted into chloride of barium, so that the chloride of alkaline metal obtained always contains a certain portion of this salt.

DECOMPOSITION OF SILICIOUS COMPOUNDS BY NITRATE OF  
BARYTA.

Nitrate of baryta was formerly employed instead of carbonate of baryta to effect the same object, but the use of this salt presents greater difficulties still. The nitrate of baryta is decomposed during the ignition, and it is the pure baryta left which alone decomposes the silicious compound. As pure baryta, however, has an action upon platinum crucibles at a red heat, the operator is under the necessity to effect the decomposition in a silver crucible; now a vessel of that metal cannot bear a very strong heat, and moreover, when most of the ignited mass has been removed from the crucible, by softening it with water, and muriatic acid is employed to detach it completely from the sides, the silicic acid set at liberty is afterwards found to be contaminated by chloride of silver. The most awkward part of this method, however, is that the nitrate of baryta, when decomposed by heat, swells up and passes with extreme facility over the edge of the crucible. The best manner of guarding against this difficulty consists in first submitting the nitrate of baryta, by itself, to a temperature sufficient to prevent its subsequent decrepitation, pulverising it, mixing it then with the silicate, heating the silver crucible containing the mixture upon an argand spirit-lamp, very gently at first, and then gradually increasing the temperature until the mass has ceased to swell and the nitrate is almost entirely decomposed; the crucible is then put upon ignited charcoal, and the heat is urged to the highest temperature that the crucible can bear without fusing. When the mass has cooled it is treated absolutely in the same manner as if, instead of nitrate of baryta, carbonate of that base had been employed.

As nitrate of baryta can be fused, the complete decomposition of the substance submitted to analysis can be thus more easily effected, especially because the baryta liberated by the ignition exerts a more powerful action than carbonate of baryta. But this method is only applicable to such substances as cannot be

conveniently attenuated by levigation, such as mica, for example, or such substances as resist the action of carbonate of baryta.

The silver crucible employed must be very strong, for if thin, the action of the red heat might crack it, and a portion of the fused mass would ooze out through the crevices.

#### DECOMPOSITION OF SILICIOUS COMPOUNDS BY FLUOR SPAR.

Berzelius was the first to propose fluor spar as a means of determining the quantity of fixed alkalis in the silicious compounds which cannot be decomposed by acids. The *modus operandi* is as follows :—The silicious compound is first reduced into very fine powder by levigation, and mixed very intimately in a platinum capsula, or in a large crucible of the same metal, with about five parts of fluor spar, which must be free from all foreign metals. It is not necessary to levigate the fluor spar, and it is sufficient to pulverise it well. The whole is then mixed with concentrated sulphuric acid by means of a platinum spatula, to creamy consistence. The capsula is gradually heated, which produces a disengagement of hydrofluoric and fluosilicic gases. The heat is then increased to incipient redness, in order to expel the free sulphuric acid. The silicic acid of the substance under examination will be found to have volatilised. If the compound contains alumina, it will have combined with the sulphuric acid, but as the ignition, as above said, will have expelled the greater part of this acid, the greatest portion of the alumina remains in an insoluble state, when the residuum comes to be treated by water.

As it is sometimes important to determine the quantity thereof, after having volatilised the sulphuric acid, the residuum is uniformly moistened with muriatic acid, which should be left to act for an hour or more. The whole is then removed into a glass by washing it out with water; more water is added, and the whole is left to digest for a long time. That which remains in an insoluble state consists principally of sulphate of lime, which is collected on a filter and washed.

In order to ascertain whether the residuum has been sufficiently washed, when the substance under examination contains alumina, ammonia is added to the water used for washing which has filtered last. If a precipitate appears, the washing must be resumed, and continued until, by washing with ammonia, the presence of this earth ceases to be indicated. The water used for washing must not be thrown away, but should be added to the filtered muriatic acid liquor. This filtered muriatic acid liquor is supersaturated with ammonia, and the precipitate produced is collected as rapidly as possible upon a filter, in order that it may not be contaminated by carbonate of lime. As, however, the quantity of sulphate of lime contained in the solution is considerable, it is difficult, in presence of the excess of ammonia contained in the liquor, to avoid all formation of carbonate of lime. The precipitate contains the whole of the alumina and of the peroxyde of iron; the quantity of both are determined, in order to compare them with those which have been obtained in the other analysis, when the substance was decomposed by carbonate of potash. The operator must not forget that the precipitate almost always contains lime; it is therefore necessary to dissolve it in muriatic acid. The alumina and peroxyde of iron are reprecipitated from this solution by means of ammonia.

In pouring oxalate of ammonia in the liquor filtered from the alumina and peroxyde of iron, the lime of the sulphate of lime in the solution is thereby precipitated. The liquor filtered from the precipitate of oxalate of lime is evaporated to dryness, and the dry residuum is ignited. The alkali remains in the state of acid sulphate, which is treated by carbonate of ammonia.

The ignition of the dry mass is not so difficult in this analysis, because the quantity of sulphate of ammonia is generally less considerable than when the substance has been treated by carbonate or by nitrate of baryta.

\* This method is more suitable to show qualitatively that the silicious compound contains an alkali, than to determine its quantity.

## DECOMPOSITION OF SILICIOUS COMPOUNDS BY HYDROFLUORIC ACID.

If the operator possesses a platinum retort, hydrofluoric acid may be employed for determining the quantity of the fixed alkalies contained in the silicates which cannot be decomposed by acids. The use of hydrofluoric acid is much more advantageous than that of fluor spar, because not only can the silicic acid be thus determined, but also all the constituents of the substance, not even excepting lime. This method, which Berzelius was also the first to recommend, is likewise that which gives the most accurate results, and the analysis goes on much more rapidly than with fluor spar, because, in the latter case, the considerable proportion of sulphate of lime produced requires an exceedingly long time for its complete removal by washing. When this method is resorted to, the hydrofluoric acid employed must be very concentrated, and recently prepared, because, by keeping, this acid soon loses its strength.

For the preparation of hydrofluoric acid, the operator takes fluor spar, which must be completely free from all foreign metallic substance, especially from copper pyrites, and reduced to powder. It is then placed at the bottom of the retort, the upper part of which is, for the time, removed, and sulphuric acid is poured on it in sufficient quantity to form a thick pap after stirring it with a platinum spatula. The upper part of the retort is then replaced, and its neck is plunged into a platinum crucible containing a little water. The neck must reach the liquor in such a way that part plunges under it, and another part is above it. The acid is distilled by the heat of a small spirit-lamp, and is continued until the aqueous acid in the crucible emits thick fumes after the removal of the retort; for the complete decomposition of the silicious compound submitted to analysis can be decomposed only by a fuming acid.

This acid is poured little by little upon a weighed quantity of the substance reduced into extremely fine powder. It is best to

perform this experiment in a large platinum capsula, for the action is so strong, that the acid ordinarily enters into ebullition, and spirts about, which, if a very small vessel were employed, might cause a loss. The whole is frequently stirred with a platinum spatula, and sulphuric acid is then cautiously added; the whole is afterwards evaporated to dryness, at a temperature which at first must be very gentle, and which is augmented by degrees. At the beginning there is a disengagement of fluosilicic and of hydrofluoric gases. The excess of sulphuric acid requires for its volatilisation a higher heat which must be carried to incipient redness. After cooling, the dry mass is moistened with concentrated muriatic acid; when the reaction has lasted long enough water is added, which dissolves the whole, except a slight residuum of silicic acid, which, owing to the presence of water, would not escape in the shape of fluosilicic gas. Whilst filtering, it often occurs that the silicic acid passes with the liquor through the paper; but when the operator has taken care to warm the liquor previously, it ordinarily filters very well. It is often necessary, however, to filter the liquor several times in succession, to separate the silicic acid completely. The powder is dried, ignited, weighed, and the weight is deducted from that of the substance operated upon. This powder may likewise be again treated by hydrofluoric acid, in order to dissolve it completely. It is not necessary then to filter it, and the operator merely decants carefully the supernatant liquid.

The filtered sulphuric acid, and muriatic acid solution now contains all the constituents of the substance under examination, except silicic acid, and it is analysed in the same manner and method which has been several times described before. When the substance contains lime, it may also be determined in a complete manner. As, however, sulphate of lime is sparingly soluble in water, the insoluble residuum must be washed until the whole of this salt is removed.

By this method, the alkali may be very easily and very accurately determined, because the quantity of sulphate of

ammonia to be separated from the bisulphate of alkali by volatilisation is always very small.

This method was modified by Laurent in the following manner:—The mineral powder is mixed with water, through which the vapours of hydrofluoric acid are passed. This modification in most cases does not appear to be a real improvement, for it might sometimes happen that a small proportion of the powder would remain in the neck of the retort in an undecomposed state.

All silicious compounds are not completely decomposed by hydrofluoric acid, but whether the decomposition is complete or not may be immediately detected by pouring the fuming acid upon the combination, which will, in the latter case, produce a strong reaction, and a great disengagement of heat. It is probable that those substances which resist the action of carbonate of potash resist also that of hydrofluoric acid. When the quantity of the fixed alkalies has to be determined in such substances, carbonate of baryta must be employed, as will be said farther on.

A lead retort must not be employed to prepare the hydrofluoric acid required for these analyses, for it would then be impossible to avoid protoxyde of lead from being held in solution in the acid. Yet the lower part of the retort may be made of lead, but the upper part must be of platinum.<sup>1</sup>

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<sup>1</sup> Instead of a platinum retort, Brunner's apparatus, which is much less expensive, may be employed with perfect success: it consists of a lead capsula, with a flat bottom, 6 inches in diameter, and  $2\frac{1}{2}$  inches high, in the middle of which there is a small ring, on which a platinum capsula is placed. This ring may be easily made with a piece of lead, from 1 to  $1\frac{1}{4}$  inch in diameter, and  $1\frac{1}{2}$  inch thick. The lead capsula has a lead cover. When a silicate has to be analysed in this manner, by means of hydrofluoric acid, it must be first reduced to powder, and put in the platinum capsula. On the other hand, a layer  $\frac{1}{4}$  an inch thick of pulverised fluor spar is put on the lead capsula, and sulphuric acid is poured upon it. The substance to be analysed which is in the platinum capsula, is then moistened with a little water, and the platinum capsula is then put on the lead ring, and the lead cover is

The decomposition of silicious compounds by hydrofluoric acid being so much more advantageous than the other methods, it is advisable, in a great number of cases in which it is desirable to obtain accurate results, to submit to its action such silicious compounds as resist the action of muriatic acid, even those which do not contain fixed alkalies, provided the operator has in his possession a platinum retort for preparing the hydrofluoric acid. But it is well also, in such a case, to decompose another portion of the substance by carbonate of potash, in order to obtain immediately the quantity of the silicic acid, and not to determine it merely from the loss.

DECOMPOSITION OF SILICIOUS COMPOUNDS BY HYDRATE OF POTASH OR OF SODA, OR BY CARBONATE OF BARYTA, WITH THE HELP OF A WHITE HEAT.

I have to speak now of the analysis of silicious compounds which resist the action of carbonate of potash. Amongst those found in nature, a few only belong to this class, and are remarkable for their extreme hardness, and consequently their pulverisation in an agate mortar presents difficulties, because during the operation a portion of the mortar itself, which it is difficult to determine, mixes with the powder; as, however, almost all the substances in question appear not to be attacked by hydrofluoric acid, the latter acid may be used in a dilute state to dissolve the portions which have been abraded from the mortar, and which may be looked upon as being pure silicic acid; there remains nothing else than the substance to be analysed. The dry powder is put in a platinum capsula, the acid is poured upon it, the whole is stirred with a platinum spatula, and when the powder has settled, the supernatant

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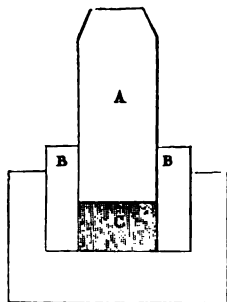
put on the whole; after which heat is applied by means of a small spirit-lamp. The experiment should be performed under the chimney-hood with a good draft, or else in the open air: 30 grains of the pulverised silicate require about two hours' treatment for their complete decomposition.

In order to prevent the substance from agglomerating into a mass, it should be stirred now and then, and moistened with a little water. The decomposed mass should be treated afterwards by sulphuric acid.—En.



liquor is decanted. The powder is then washed with water until it ceases to redden blue litmus paper. The powder being thus well washed is dried.

\* In order to divide such hard substances, the operator may also use a steel mortar, which was first described by Abich. All the parts of this mortar are forged out of the best English steel, perfectly polished, and fit each other exactly.



A is the pestle, fitting exactly the ring B, but capable of moving freely up and down. The ring is slightly conical, and fits the mortar accurately, but can likewise move freely up and down like the pestle. The lumps which the operator wishes to crush are put in C, and the pestle is put over it and struck by a slight blow with a wooden mallet; it is lifted a little and again struck. By repeating this several times, taking care also to strike the sides of the mortar now and then, the substance spreads over the interior surface of the mortar, and all loss from the shifting of the ring is at the same time avoided. The powder gradually acquires a great degree of comminution.

The powder thus obtained is then digested with dilute muriatic acid, in order to free it from any particles of steel which may have been abraded during the operation, and which never exceeds one-half or one per cent.

Hydrate of potash is generally employed for the decomposition of these substances, but its employment is attended with

great difficulties. Ordinarily it is not the dry hydrate which is employed, but after having put in a dry silver crucible the substance reduced to very fine powder by levigation, a concentrated solution of potash of a known strength is poured upon it, and the whole is evaporated to dryness, taking care diligently and incessantly to stir the whole with a silver spatula. The dry mass is then ignited. The experiment must absolutely be executed in a silver crucible, because hydrate of potash has too strong an action upon those of platinum. The mass spirts during the ignition, owing to which only a gentle heat must be used at first, which is gradually augmented. When the ebullition has ceased, the temperature is urged to the highest point which the crucible can bear. After the ignition it is very difficult to remove the mass from the crucible. If to effect this, dilute muriatic acid is employed, the silicic acid, which is afterwards separated, contains small quantities of chloride of silver.

Berzelius fortunately succeeded in avoiding these great difficulties which attend the use of hydrate of potash, in the following manner:—The substance to be analysed is pulverised, ignited, weighed, and mixed with three times its weight of carbonate of potash or of soda in a platinum crucible, and in the middle of the mixture a small depression or cavity is formed. The crucible is then gently heated for a quarter of an hour, without fusing the mass. It is then suffered to cool, and in the small depression or cavity above mentioned, rather more than one part of hydrate of potash or of soda is placed. This done, the crucible is again heated slowly, the hydrate of alkali gradually sinks into the pores of the saline mass, without any projections taking place, which otherwise would take place on losing its water. The heat is then increased to whiteness. In this manner the crucible is not attacked, and the ignited mass is subsequently treated as if it had been decomposed by carbonate of potash.

\* According to Abich, carbonate of baryta may be employed

instead of hydrate of potash or of soda, which substance is mixed with the pulverised mass and exposed to a heat sufficient to fuse it. The powder is mixed with four times its weight of carbonate of baryta, in a platinum crucible about two inches high, and when the mixture is very intimate it is ignited upon a spirit-lamp until the agglomerated mass begins to separate. The crucible is then to be well covered and bound with a platinum wire, placed in a strong hessian crucible about four inches high, and well covered, and the whole is introduced into a blast-furnace, similar to that which was first described by Sefstroem,—it is placed therein upon a convenient support, at such a height that its lower portion is precisely in the hottest point. When the crucible has attained a moderate redness it is surrounded with charcoal up to the cover, and the furnace is then filled up with pieces of coke of a convenient size, and a continuous blast of air is kept up with the bellows. As soon as the coke has burnt to the level of the cover, the furnace is replenished with fresh coke. Experience teaches the precautions to be taken to prevent the fusion of the hessian crucible, and the platinum one which it contains, from being damaged. The moment at which the hessian crucible begins to soften, depends, of course, on the construction of the furnace, and on the management of the fire, which is matter of experience.

\* The success of the operation rests on three points, which deserve attention. First, the hessian crucible and its cover must fit each other perfectly; secondly, the blast must not be too strong; and lastly, the fusion must not be continued for more than a quarter of an hour.

\* Before the last coals have been completely consumed, it is necessary, in order to avoid the scories from adhering to the support, to withdraw the crucible and leave it to cool gradually into sand. The crucible and its cover are then so completely soldered together that they form a perfectly closed vessel, in which, upon being broken, the platinum crucible is found whole and uninjured.

\* When the experiment has been well managed, the mass is

perfectly fused; it has a crystalline surface, covered with shining scales. It is easily detached from the crucible. It is then treated by dilute muriatic acid absolutely, as was said (page 468). The solution in muriatic acid takes place without any disengagement of gas, the strong heat employed having expelled the carbonic acid from the carbonate of baryta.

\* Substances which do not contain silicic acid, and which resist the strongest reagents, may also be decomposed by this process,—such are, for example, spinel, pleonaste, gahnite, and chrome-iron.<sup>1</sup>

\* Carbonate of baryta is preferable to carbonate of potash and of soda in these experiments, because the substances in question are not so completely decomposed by the latter as by the former.

#### EXAMINATION OF THE SILICIC ACID OBTAINED IN THE ANALYSIS OF SILICIOUS COMPOUNDS.

When the silicic acid has been obtained by one of the methods which have been described before, the operator must never omit to examine whether it is really pure. This precaution must be

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<sup>1</sup> Spinel is a combination of alumina and magnesia, with a blue or a red colour; the blue is due to the presence of a very small portion of protoxyde of iron, the red to that of chromic acid. When black, it is known under the name of pleonaste (spinel ruby). An analysis of one of these varieties by Berzelius is here given:

Alumina . . . . .	72.25
Magnesia . . . . .	14.63
Silica . . . . .	5.45
Protoxyde of Iron . . . . .	4.26
	<hr/>
	96.59

In all these compounds, the silica is looked upon as an accidental ingredient. Chrome-iron has been mentioned before.

Gahnite is a combination of alumina and zinc. The analysis by Abich, of that of Haerlem, in Sweden, yielded,—

Alumina . . . . .	55.14
Silica . . . . .	3.84
Oxyde of Zinc . . . . .	30.02
Protoxyde of Iron . . . . .	5.85
Magnesia . . . . .	5.25

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100.10—ED.

observed especially in the analysis of those substances which are not easily decomposed by carbonate of potash. The test employed, and to which might be submitted the small quantities of silicic acid which have separated when the other constituents have been dissolved in muriatic acid, consists in fusing with the blowpipe, a little of the said silicic acid with soda, upon charcoal. If the glass thus obtained is liquid and colourless the silicic acid is pure or at least does not contain a very large proportion of other substances.

This test is often sufficient in the analysis of the silicious compounds which are easily decomposed by carbonate of potash, because the silicic acid obtained in such cases is almost always pure. But when the substance is difficult to decompose, and can be effected only by hydrate of potash, the silicic acid must be examined with great care. In such cases it may still retain a considerable proportion of alumina, the presence of which cannot be detected by the above said test, for the glass obtained by fusion with soda may remain transparent, though a large quantity of alumina may be present. The quantity of the alumina contained in the silicic acid often amounts to 12 or 15 per cent.; and, notwithstanding this considerable admixture, the glass may remain limpid after fusion with soda. In such a case, the operator should never omit to fuse a portion of the silicic acid obtained with a considerable quantity of carbonate of potash, and to treat the fused mass by muriatic acid, and to evaporate the liquor to dryness. The dry mass is then moistened with muriatic acid, and then treated by water, the muriatic acid liquor is then filtered from the silicic acid, which has not dissolved, and it is supersaturated with ammonia; if it remains perfectly clear, the operator may conclude that the silicic acid was pure, but if a precipitate appears it can only arise from the presence of a foreign substance, which was united with the silicic acid, and which in most cases is alumina, for it is especially when silicious compounds contain too much alumina that they become difficultly decomposed in a complete manner by carbonate of potash.

\* The silicic acid obtained from the combinations which have been decomposed by muriatic acid is that the purity of which requires more especially to be carefully examined, when the decomposition of the substance has not been complete, or when the substance was intimately mixed with small quantities of other silicious combinations, which could not be separated completely by levigation in the manner described (page 454). The whole of these substances is formed in the liberated silicic acid, from which they may, however, be very easily separated by treatment with a solution of carbonate of potash or of soda. After having ignited and weighed the silicic acid, a solution of carbonate of alkali is poured upon it, and the whole is boiled. This operation is best performed in a platinum capsula. After boiling the liquor is suffered to cool. If the entire mass of the silicic acid has dissolved, this acid was perfectly pure; but if all has not dissolved the operator waits some time, so that all the insoluble substances may settle well at the bottom; the clear liquid is then decanted, and the residuum is boiled with a fresh quantity of carbonate of potash or of soda, until that which remains refuses to dissolve altogether. This residuum is then collected on a filter, washed, and its weight is determined, which is then deducted from that of the silicic acid. It is necessary in this experiment to employ a pretty large excess of alkaline carbonate, in order that the solution should not on cooling stiffen into a jelly.

\* The silicic acid which has been separated from combinations which can be decomposed only by fusion with an alkaline carbonate, may also be submitted to this test when the decomposition of the substance by carbonate of alkali is difficult. But the operator cannot thus detect whether it contains alumina. This can only be ascertained by the method which has been described before, because alumina is capable of being dissolved by boiling with a concentrated solution of carbonate of fixed alkali. It is easy, by the methods which have been indicated before, to separate silicic acid from most of the bases. I have

already said in the first volume of this work, that in most of the native silicates, the silicic acid is almost always combined with the same bases. These bases are alumina, lime, magnesia, protoxyde of iron, a greater or less quantity of protoxyde of manganese, and an alkali. As they are all soluble in muriatic acid, they are constantly found in the muriatic acid solution, which was filtered from the silicic acid. If the base of an artificial silicious compound does not dissolve in muriatic acid, as is the case, for example, with oxyde of silver, and protoxyde of lead, then, instead of muriatic acid, nitric acid is employed as was said before. In those cases only in which silicic acid has to be quantitatively separated from a small number of bases, and of acids which exist in a few native silicates, particular precautions have to be taken, but which cannot as yet be mentioned here.

#### SEPARATION OF WATER IN SILICIOUS COMPOUNDS.

\* A great many native silicious compounds contain water. All those which are in this predicament can be decomposed by muriatic acid. Generally the quantity of the water is determined from the loss sustained by igniting a certain weighed quantity of the substance in a platinum crucible. Very often, however, the ignition renders the substance incapable of being afterwards decomposed by muriatic acid. Wherefore, the rest of the analysis must be performed upon another portion of the combination. But if the operator possesses only a small quantity of it, for example, one or two grammes, and has to determine all the constituents by one single operation, the quantity of the water is first determined as we said, and the compound is subsequently decomposed either by muriatic acid or by carbonate of potash.

#### SEPARATION OF PHOSPHORIC ACID FROM SILICIOUS COMPOUNDS.

When a silicious compound contains phosphoric acid, and can be decomposed by muriatic acid, the whole of the first of these

two acids is contained in the liquor filtered from the silicic acid along with the bases which were combined with it and with the silicic acid. These bases are separated from the phosphoric acid by the methods which have been indicated in the preceding chapter. Yet it is better at once to mix and fuse the silicious compound with three or four times its weight of carbonate of potash or of soda, in a platinum crucible. If the combination cannot be decomposed by muriatic acid, the powder, after having been levigated, must always be submitted to this treatment. Water is poured upon the fused mass, and that which has refused to dissolve is separated by filtering, and washed with water. The solution contains then the phosphoric acid combined with the potash or soda, and with the excess of carbonate of potash employed. The insoluble residuum consists of silicic acid and of the bases which exist in the combination which has been analysed. Yet, a small portion of silicate of potash has dissolved at the same time. Wherefore, a little carbonate of ammonia is added to the solution, and it is slightly evaporated, which produces a separation of light flocks of silicic acid, which are collected on a filter, washed, and added to the mass which the water has not dissolved. Muriatic acid is then poured upon the whole residuum, which is thus easily decomposed. The silicic acid then separates under the form of a jelly, but in order to obtain the whole of it the solution is evaporated to perfect dryness in a platinum capsula, which renders the silicic acid altogether insoluble. The dry mass is then uniformly moistened with muriatic acid, and water is poured upon it. The undissolved silicic acid is collected on a filter, and the quantity of the bases in the filtered liquor is determined.

It is best to collect on a filter the mass which refused to dissolve in the water, and, after having washed it well, to pour muriatic acid upon it whilst on the filter, for after drying it is difficult to detach it completely from the filter without loss. It is true that the silicic acid subsequently turns black upon being ignited on account of the carbon liberated, but its white colour



is restored by continuing the calcining a little longer with the contact of the air.

In that case the quantity of the phosphoric acid has now to be determined. The liquor filtered from the residuum is super-saturated with muriatic acid, which must be done with care, for fear of loss by reason of the effervescence which takes place; and a too large excess of muriatic acid must also be avoided. It is best to effect this saturation in a large porcelain or platinum capsula. The acid liquor is then left at rest for twenty-four hours, covering it only with filtering paper, during which the free carbonic acid has time to be disengaged. For greater safety, the liquor may further be heated or boiled. This being done, it is poured in a bottle capable of being closed; it is super-saturated by ammonia, and solution of chloride of calcium being added, the bottle is corked up. The phosphoric acid is thus precipitated in the state of phosphate of lime. The bottle is left at rest until the precipitate has settled well, and the supernatant liquor is rapidly filtered, after which the precipitate itself is thrown upon the filter, and rapidly washed. The atmospheric air having been excluded during the precipitation of the phosphate of lime, it cannot be contaminated by carbonate of lime. When perfectly dried, it is ignited, and its weight is determined. It is afterwards decomposed by sulphuric acid, and weak alcohol is further added. The weight of the sulphate of lime produced indicates the quantity of dry phosphoric acid.

If the substance submitted to analysis contains phosphoric acid, a large quantity of alumina, and only a very small proportion of silicic acid, it is necessary, before fusing it with the alkaline carbonate, to add a sufficient quantity of silicic acid, so that the ignited mass may contain about one part and-a-half of silicic acid and two parts of phosphate of alumina. The silicic acid which is thus added must have been previously ignited in a platinum crucible, and weighed most accurately after cooling. The weight thus added is subsequently deducted from the silicic acid obtained in the analysis.

\* In such a case the quantity of the phosphoric acid is better determined by acidifying the liquor with acetic acid, and after the carbonic acid has disengaged, adding a solution of acetate of lead. The quantity of the phosphoric acid contained in the phosphate of lead which precipitates must likewise be determined (page 431).

SEPARATION OF SULPHURIC ACID, AND OF SULPHUR, IN SILICIOUS COMPOUNDS.

When sulphuric acid is contained in the silicious compound under examination, and if this silicious compound previously pulverised can be decomposed by muriatic acid, the whole of the sulphuric acid may be found in the liquor filtered from the silicic acid. It is precipitated by means of a solution of chloride of barium, and from the quantity of sulphate of baryta obtained, the quantity of the sulphuric acid is determined in the usual manner. Sulphuric acid is now added to the filtered liquor in order to precipitate the excess of baryta, and the bases which exist in the combination are afterwards determined.

If the silicious compound containing sulphuric acid cannot be decomposed by muriatic acid, it is reduced into fine powder by levigation, and fused with carbonate of potash or of soda. The ignited mass is treated by water, which dissolves the sulphate of alkali produced in the preceding operation and the excess of carbonate of alkali. The solution is moderately acidified by adding muriatic acid thereto, and the sulphuric acid is precipitated therefrom by a solution of chloride of barium. That which remains undissolved is decomposed by muriatic acid. The precautions which have been indicated for the analysis of the substances which contain phosphoric acid, and which have just been enumerated, must be adopted here also.

When the silicious compound submitted to analysis contains sulphur combined with a metal in the state of metallic sulphuret, and if this substance can be decomposed by muriatic

acid, the best is to reduce it into powder, and to treat it by fuming nitric acid, as has been said (page 375.) All the sulphur is thereby converted into sulphuric acid. The silicic acid is first separated by filtering, and the remainder of the process is the same as has been described. C. G. Gmelin has employed this method for the analysis of *helvine*.<sup>1</sup>

\* Instead of fuming nitric acid it may also, after having previously reduced it to powder, be intimately mixed and fused with a mixture of nitrate and of carbonate of alkali. The fused mass is softened by water, and treated as has been said (page 487), when speaking of the determination of phosphoric acid in silicious compounds. The liquor filtered from the undissolved combination of silicic acid with the bases is saturated with muriatic acid, and, by means of a solution of chloride of barium, the sulphuric acid is precipitated in the state of sulphate of baryta. The undissolved portion is treated as has been said above. This method is particularly applicable when the decomposition of silicious compounds by muriatic acid is difficult or impossible.

If the silicious compound which can be decomposed by muriatic acid contains sulphuric acid, and a metallic sulphuret, a certain quantity of it is treated by fuming nitric acid, and after having separated the silicic acid by filtering, the quantity of the sulphuric acid contained in the combination and that produced by the oxydisation of the metallic sulphuret is determined by means of a solution of chloride of barium. The operator then takes another weighed portion of the combination,

<sup>1</sup> Helvine is a combination of silica, glucina, and alumina, with the protoxydes of iron and manganese. That of Schwartzberg, analyzed by Gmelin, yielded,—

Silica . . . . .	35.27
Alumina . . . . .	1.45
Glucine . . . . .	8.02
Protoxyde of Manganese . . . . .	29.35
Protoxyde of Iron . . . . .	7.99
Sulphuret of Manganese . . . . .	14.00

it is pulverised, and treated by muriatic acid, which ordinarily decomposes the metallic sulphuret with disengagement of sulphuretted hydrogen. After having separated the silicic acid by filtering, the sulphuric acid is precipitated from the filtered liquor, and the quantity obtained being subtracted from that which was obtained in the other analysis by means of nitric acid, the operator knows how much of this acid was produced by oxydisation. A precaution which it is important to take in this operation consists in avoiding, as much as possible, the contact of the air during the decomposition by muriatic acid, and to filter it as soon as possible afterwards, in order to separate the silicic acid, and to precipitate the sulphuric acid promptly.

#### SEPARATION OF OXYDE OF CHROMIUM FROM SILICIOUS COMPOUNDS.

When a silicious compound contains oxyde of chromium, and can be easily decomposed by muriatic acid, its analysis is not difficult. The oxyde of chromium is then found with the other bases in the liquor, separated from the silicic acid by filtering, and it is separated from the other bases by the methods which have been described before.

When the combination cannot be decomposed by muriatic acid, it is ignited in the ordinary way with carbonate of potash in a porcelain crucible. The calcined mass is afterwards supersaturated in a glass with muriatic acid, and the whole is heated. The chromic acid which has formed during the ignition is thereby converted into chromic oxyde. In order to accelerate the reduction, it is advisable to add a little alcohol to the muriatic acid. The silicic acid, separated in the ordinary manner, is not white, according to Trolle Wachtmeister, but has a dark brown tinge, due to the presence of some chromium. In order to obtain it in a perfectly pure state, it must be ignited again with carbonate of potash in the platinum crucible, as was done for the silicious compound, the ignited mass is treated by muriatic acid and alcohol, the whole is evaporated to dryness, and the dry residuum is moistened with muriatic acid; the silicic acid

is then left in a pure state after treatment by water. The filtered liquor, which contains oxyde of chromium, is mixed with that which was obtained before. The oxyde of chromium, together with some peroxyde of iron, or sometimes also with alumina, is afterwards precipitated; and it is separated from the two latter substances by the method which has been described (pages 322—327).

#### SEPARATION OF SILICIC ACID FROM VANADIC ACID.

\* Vanadic acid clings to silicic acid more obstinately than to any other substances. This combination is soluble in acids and in alkalies, and when silicic acid has been once separated by the action of the latter, it is as soluble as that which is precipitated from fluoride of silicium by water.

\* Silicic acid cannot be separated from vanadic acid in any other manner than by pouring concentrated sulphuric acid upon the combination of the two acids, and adding hydrofluoric acid thereto, volatilising the latter in conjunction with the silicic acid, and, lastly, increasing the heat, in order to expel the sulphuric acid. The pure vanadic acid remains behind.

#### SEPARATION OF VANADIC ACID AND PHOSPHORIC ACID FROM SILICIC ACID.

\* Vanadic acid forms with phosphoric and silicic acids combinations which crystallise, are soluble in water, and may be analysed in the following manner:—The operator first begins by determining the water of crystallisation, by gently heating the compound, which is afterwards treated by a solution of carbonate of ammonia; the silicic acid remains, and its quantity is determined. The vanadate of ammonia is separated from the phosphate as has been said (page 429).

#### SEPARATION OF TITANIC ACID FROM SILICIOUS COMPOUNDS.

The separation of silicic acid from titanic acid is attended with great difficulties.

If the combination containing both substances is decomposable by muriatic acid, it is digested with this acid, after having previously reduced it to powder, or even levigated it if necessary. The digestion must take place in the cold, or, at any rate, at such a gentle heat as should not cause the separation of the titanic acid from its solution in the muriatic acid, because when once liberated, it no longer redissolves in any excess whatever of muriatic acid. When the combination is entirely decomposed, the silicic acid is separated by filtering, and its quantity is determined. The titanic acid is afterwards separated from the filtered liquor by means of ammonia. The small portion of silicic acid which has dissolved in the muriatic acid simultaneously with the titanic acid, cannot be determined here except with difficulty, but it is very slight, and cannot be above one per cent.

In this operation the operator must take care to wash the silicic acid with cold water only, and not with hot water; but it is especially important that the heat should be as gentle as possible, during all the time that the digestion in muriatic acid lasts, because otherwise, a little titanic acid would be precipitated, and could not be redissolved in this acid.

The difficulties are greater still when the separation of silicic acid from titanic acid has to be effected in combinations which are not attacked by acids. The following method must then be adopted: The combination is reduced into fine powder by levigation, fused in a platinum crucible with carbonate of potash or of soda, as has been said above. Dilute muriatic acid is poured upon the fused mass, and an excess of the same acid being afterwards added, the liquor is diluted with water. The fused substance then dissolves. Heat must not be applied to promote the action of the acid upon the fused mass. Flocks of undissolved silicic acid remain, still their greater or less abundance depends on the greater or less quantity of carbonate of alkali with which the combination was fused, and on the greater or less degree of dilution of the acid which was added. The titanic

acid is dissolved entirely. The silicic acid which has remained insoluble is collected on a filter, and washed with cold water. The filtered liquor is supersaturated with ammonia, which precipitates the titanic acid along with the silicic acid. The precipitate is collected on a filter, and washed with cold water; it is afterwards thoroughly dried, which must be done altogether in the air, and not in a warm place. After drying, this precipitate is put to digest in cold concentrated muriatic acid; the titanic acid dissolves whilst the silicic acid remains insoluble. As soon as the solution of the titanic acid is finished, the silicic acid is separated by filtering, and washed with cold water. The acid solution of the titanic acid must not be left long with the undissolved silicic acid, because some titanic acid might, in course of time, separate. The titanic acid is afterwards precipitated from the filtered liquor by means of ammonia. The precipitate is dried, ignited, and its weight is determined.

The liquor which has been filtered from the precipitate, which consists of the silicic and titanic acids, contains still a small quantity of silicic acid and all the constituents of the substance under examination and which cannot be precipitated by ammonia. In order to separate the silicic acid, the liquor is supersaturated with muriatic acid, and evaporated to dryness.

When, however, the combination submitted to analysis contains substances which can be precipitated with titanic acid by ammonia, such as peroxyde of iron, the analysis becomes more difficult still. These substances dissolve with the titanic acid in the muriatic acid, and they are separated in the solution, in the manner which has been described (page 278).

After having precipitated together the silicic and the titanic acids by ammonia, if the substance contains lime, it must be filtered as rapidly as possible, and out of the contact of the air. The lime contained in the filtered liquor is separated therefrom by pouring the solution of an oxalate into it.

It is necessary to ascertain that the silicic acid obtained is

free from titanitic acid. This can be done by means of the blow-pipe, by keeping for a long time the acid mixed with microcosmic salt in the interior flame upon charcoal. The presence of the titanitic acid is detected by the bluish or violet colour which the fused bead assumes on cooling.

#### SEPARATION OF PEROXYDE OF TIN FROM SILICIOUS COMPOUNDS.

It very frequently happens that silicious compounds contain small quantities of peroxyde of tin. When such silicious compounds cannot be decomposed by muriatic acid, the operator is, on that account, obliged to employ carbonate of alkali to effect their decomposition; it sometimes happens that the silicic acid liberated retains a little peroxyde of tin; sometimes even the peroxyde of tin is combined with an earth besides, especially with glucina, when the latter substance is one of the constituents of the compound submitted to analysis. It is very easy to obtain these small quantities of peroxyde of tin by digesting the silicic acid in hydrosulphuret of ammonia before igniting it; the tin is thereby dissolved.

The best method of effecting this digestion consists in smearing the neck of the funnel upon which the silicic acid has been filtered with a pretty thick coating of tallow, and to put it upon a small flask with a narrow neck, which it must fit, so as to close it hermetically; hydrosulphuret of ammonia is then poured upon the silicic acid, with which it remains in contact for a long time, because it is thus prevented from filtering through. When the operator believes that the whole of the tin has dissolved, the funnel is removed from the flask, and the liquor contained therein is then allowed to filter. The solution of the tin is evaporated to dryness, and the dry mass is strongly ignited. In this manner the smallest quantities of sulphuret of tin are converted into peroxyde of tin.

When the peroxyde of tin has been previously dissolved in muriatic acid, the best method of precipitating it from the acid



liquor, which was filtered from the silicic acid, consists in passing a current of sulphuretted hydrogen through the latter; the small quantity of sulphuret of tin thus produced is afterwards calcined, by which means it is converted into peroxyde of tin.

#### SEPARATION OF PROTOXYDE OF COPPER IN SILICIOUS COMPOUNDS.

When a silicious compound contains protoxyde of copper, it is best, after having separated the acid solution from the silicic acid by filtering, to precipitate the oxyde in question by means of sulphuretted hydrogen, and to treat the sulphuret of copper thus produced, as has been said (page 188).

If the quantity of protoxyde of copper existing in the substance is inconsiderable, as for example, in the cupriferous idocrase of Norway,<sup>1</sup> it sometimes happens that it is overlooked when it is not immediately precipitated after the separation of the silicic acid. After having filtered the liquor from the sulphuret of copper, it is heated in order to expel the sulphuretted hydrogen which it holds in solution, and if protoxyde of iron is present, it is converted into peroxyde of iron.

#### SEPARATION OF OXYDE OF URANIUM IN SILICIOUS COMPOUNDS.

\* When these combinations can be decomposed by muriatic acid, the liquor is filtered in order to separate the silicic acid, and by pouring ammonia into it, the oxyde of uranium, conjointly with peroxyde of iron and alumina, if these two substances exist in the compound, are precipitated. The oxyde of uranium is afterwards separated from the two latter substances,

<sup>1</sup> The idocrase found at Egge, near Christiansand in Norway, has been analysed by Magnus, who gave the following results :

Silica . . . . .	37·658
Alumina . . . . .	17·695
Lime . . . . .	31·896
Protoxyde of Iron . . . . .	4·537
Magnesia . . . . .	6·489
Protoxyde of Manganese . . . . .	0·499
	<hr/>
	98·774

after previously dissolving the precipitate in muriatic acid by adding carbonate of ammonia to the liquor.

#### SEPARATION OF PROTOXYDE OF LEAD IN SILICIOUS COMPOUNDS.

\* The native silicates contain only traces of protoxyde of lead. If the combination can be decomposed by muriatic acid, the current of sulphuretted hydrogen is passed through the liquor filtered from the silicic acid, by which means the protoxyde of lead is precipitated in the state of sulphuret of lead, otherwise its presence might be overlooked afterwards. If the lead is accompanied by iron, the protoxyde of iron is converted into peroxyde of iron in the liquor which has been filtered, to separate it from the sulphuret of lead.

\* If, on the contrary, a silicious combination containing a very large quantity of lead were treated by muriatic acid with a view to decompose it, the chloride of lead formed might remain with the silicic acid, from which it could not be separated, except by a protracted washing. It is better, therefore, after having pulverised the substance to decompose it, not by muriatic, but by nitric acid, and after having removed the silicic acid, to precipitate the protoxyde of lead from the solution by sulphuretted hydrogen.

When a silicious compound containing much lead is difficult to decompose, or cannot be decomposed at all by nitric acid, it is ignited with carbonate of potash or of soda in a platinum crucible. The heat must not be too strong, nor continued too long, and care must be taken that no carbon or organic matter find their way to the mixture, because a little of the oxyde might thus be reduced. The ignited mass is then softened with water, supersaturated with nitric acid, and the whole is evaporated to dryness, in order to obtain the silicic acid. The dry mass is then moistened with nitric acid, and shortly afterwards water is added; the silicic acid is then collected on

a filter. The first thing to be done with respect to the filtered liquor is to precipitate the protoxyde of lead therefrom by means of sulphuretted hydrogen.

SEPARATION OF OXYDE OF CADMIUM FROM SILICIOUS  
COMPOUNDS.

\* Sulphuretted hydrogen is the reagent employed to precipitate the oxyde of cadmium in the state of sulphuret of cadmium, exactly as when the combination contains protoxyde of copper or protoxyde of lead. The sulphuretted hydrogen is passed through the filtered muriatic acid liquor immediately after having separated the silicic acid.

SEPARATION OF OXYDE OF NICKEL IN SILICIOUS COMPOUNDS.

\* The best method of determining small quantities of oxyde of nickel in silicious compounds consists, after having separated the silicic acid from the muriatic acid solution, in adding carbonate of potash or of soda to the latter almost to saturation, and to heat it afterwards with a solution of pure potash, which dissolves the alumina, but precipitates the oxyde of nickel and peroxyde of iron, which may subsequently be separated from each other in the manner indicated (page 152). If magnesia be present besides, the separation of the two oxydes presents more difficulties, and the analyst must operate as was said (page 153).

SEPARATION OF OXYDE OF ZINC IN SILICIOUS COMPOUNDS.

\* In the analysis of these combinations, and after having separated the silicic acid, a current of sulphuretted hydrogen is passed through the filtered muriatic acid liquor, in order to precipitate in the state of metallic sulphurets all the oxydes which may be thus precipitated, such as, for example, oxyde of cadmium, &c. The liquor is then filtered, the protoxyde of iron is then converted into peroxyde of iron, and the peroxyde of iron and alumina, if present, are separated from the oxyde of zinc, as was said (pages 118—119).

**DETERMINATION OF QUANTITIES OF PROTOXYDE AND OF PEROXYDE OF IRON WHEN THEY BOTH EXIST SIMULTANEOUSLY IN SILICIOUS COMPOUNDS.**

I have already said (page 287) that it is not possible to determine the quantities of protoxyde and of peroxyde of iron accurately in a substance which resists the action of muriatic acid. This is the case with the silicious compounds, which can be decomposed only by treatment with carbonate of alkali, or by hydrate of potash, and which contain the two oxydes of iron.

When, however, these two oxydes exist in a silicious substance capable of being decomposed by muriatic acid, which is the case, for example, with the mineral called ilvaite,<sup>1</sup> the method of determining their quantity is as follows:—A portion of the compound is first reduced to powder and introduced into a bottle, which can be hermetically closed, and it is treated therein as has been said (page 107). When it has been completely decomposed, out of the contact of the air, and all has dissolved, except the liberated silicic acid, an aqueous solution of sulphuretted hydrogen is added to the liquor. After some time, when the liquid has become clear, the mixture of silicic acid and of sulphur is collected on a filter and washed; it is then perfectly

<sup>1</sup> Ilvaite forms a jelly when treated with muriatic acid: the composition of that found at Elba is, according to Kobel and Rammelsberg,—

Ilvaite from Elba.	Kobel.	Rammelsberg.
Protoxyde of Iron . . . . .	31·900	33·07
Peroxyde of Iron . . . . .	23·000	24·58
Silica . . . . .	29·278	29·83
Lime . . . . .	13·779	12·44
Oxyde of Manganese . . . . .	1·587	1·50
Alumina . . . . .	0·614	0·00
Water . . . . .	1·268	0·00
	<hr/> 101·426	<hr/> 101·42

dried, and carefully treated by fuming nitric acid, which converts the whole of the sulphur into sulphuric acid. The silicic acid is collected on a filter, and the silicic acid is precipitated from the filtered liquor, by means of a solution of chloride of barium. It is necessary to treat the silicic acid a second time by fuming nitric acid, in order to make sure that it is completely free from sulphur. From the quantity of sulphate of baryta produced that of the precipitated sulphur is calculated, from which the quantity of the peroxyde of iron contained in the combination, and which was thus reduced into the state of protoxyde, is estimated. The liquor filtered from the mixture of the silicic acid and sulphur is afterwards treated so as to convert the protoxyde of iron which it holds in solution into peroxyde of iron; the latter oxyde is then precipitated, and from its weight the quantity of the iron is determined. Lastly, the operator determines the quantity of the other substances which may have been dissolved at the same time by the muriatic acid.

Another portion of the substance is decomposed by muriatic acid, with the same precautions as before, and avoiding the contact of the air, and a solution of soda-chloride of gold is added. After a few days the insoluble residuum is collected on a filter, and which consists of a mixture of silicic acid and of gold; it is then washed, dried, ignited and weighed. This being done, the mixture is treated by aqua regia, which leaves the silicic acid in an insoluble state. The quantity of gold which accompanies the silicic acid, and which will have dissolved, may be estimated from the loss: the metal may likewise be precipitated from the solution. From the quantity of the gold, that of the protoxyde of iron in the substance submitted to analysis is calculated.

#### SEPARATION OF ZIRCONIA IN SILICIOUS COMPOUNDS.

\* The compound of silicic acid and zirconia, called zircon or hyacynth, contains these two substances in such an intimate

state of union, that they cannot be separated from each other, except by treatment with hydrate of potash, which is done in the manner described (page 478).<sup>1</sup> The ignited mass is decomposed as usual by muriatic acid; the whole is evaporated to dryness, the dry mass is moistened with strong muriatic acid, and after having added water, the silicic acid is collected on a filter. The silicic acid, even though the analysis may have been performed with the greatest care, frequently contains pretty considerable quantities of the undecomposed compound. After drying, its weight is determined. It is then put in a platinum crucible and concentrated hydrofluoric acid is poured upon it, which dissolves the silicic acid, and leaves the undecomposed compound undissolved, the weight of which is determined and deducted from that of the silicic acid. The solution of the silicic acid in the hydrofluoric acid may likewise contain a little zirconia; wherefore sulphuric acid must be poured upon it, and the liquor is evaporated until all the hydrofluosilicic acid has volatilised. The residuum is then dissolved in water, and the zirconia is precipitated from the solution by means of ammonia; its weight is determined and deducted also from the silicic acid, by which means the true quantity of the latter is thus arrived at. The presence of the zirconia is owing to this, that after the drying of the ignited mass treated by muriatic acid, a portion of the earth which had lost its acid, refused to redissolve in the muriatic acid.

\* The liquor filtered from the silicic acid is then treated by ammonia, which precipitates the zirconia. After having dried and weighed the latter substance, it can no longer be dissolved in concentrated sulphuric acid, except with the help of heat; the liquor is diluted with water, and the small quantity of silicic acid which separates is collected on a filter, and its

<sup>1</sup> The composition of zircon, or zirconite, and of hyacinth, are given by Berzelius and Muir as follows :—

	SILICONITE.	HYACINTH.
Zirconia . . .	67·16	66·00
Silica . . .	33·48	33·32
	100·64—Berzelius.	99·32—Muir.

weight is determined, in order to deduct it from that of the zirconia.

\* If the zirconia still contains any peroxyde of iron, it is separated in the manner indicated (page 94).

When the combination of zirconia and silicic acid submitted to analysis, is the mineral called eudialite, which contains, besides lime, peroxyde of iron, sesquioxyde of manganese, and soda, a portion of which latter body probably exists in the compound in the state of chloride of sodium, the substance is first decomposed, and the silicic acid is separated. Ammonia is then employed to precipitate the zirconia and peroxyde of iron, the precipitate is rapidly collected on a filter, in order to prevent its becoming contaminated by carbonate of lime, and after having redissolved this precipitate in muriatic acid, the zirconia and peroxyde of iron are separated from each other according to the method mentioned (page 94). The quantity of the lime and soda is determined afterwards in the usual manner. The quantity of the metallic chloride is determined in another portion of the combination, which for this purpose the operator must decompose by nitric acid.

#### SEPARATION OF PROTOXYDE OF CERIUM AND OF YTTRIA IN SILICIOUS COMPOUNDS.

\* These two substances appear to exist almost always simultaneously in silicious compounds. In the course of the analysis they are found, after the separation of the silicic acid, in the precipitate produced by ammonia, accompanied by peroxyde of iron, alumina, &c., from which they can be separated by the methods which have been fully described before.

#### SEPARATION OF THORINA IN SILICIOUS COMPOUNDS.

\* After having separated the silicic acid in the usual manner, ammonia is poured in the filtered muriatic acid liquor, by which

means the thorina is precipitated. The precipitate is rapidly collected on a filter, in order to prevent the formation of carbonate of lime. The precipitate produced by ammonia contains, besides thorina, several other substances which existed in the silicious compound, and which were precipitated at the same time by the volatile alkali. These are quantitatively separated from the thorina by the same means which are employed in the quantitative analysis.

#### SEPARATION OF GLUCINA IN SILICIOUS COMPOUNDS.

\* After having separated the silicic acid, the filtered muriatic liquor is treated as was said (page 60), in order to separate the glucina from alumina.

\* It sometimes happens, however, in decomposing certain silicious compounds by carbonate of potash, that the glucina forms, with certain metallic oxydes, combinations which resist the decomposing action of muriatic acid, and which, after treatment of the mass fused with carbonate of alkali by muriatic acid and by water, remain mixed with the silicic acid, from which, however, they may be easily separated, as was described in the first volume of this work, by levigation and fusion with bisulphate of potash.

#### SEPARATION OF BARYTA FROM SILICIOUS COMPOUNDS.

\* Sulphuric acid is the reagent employed to precipitate baryta from the muriatic acid liquor filtered from the nitric acid. But if the substance contains strontia besides, and a considerable quantity of lime, the precipitation should be effected by hydrofluosilicic acid. To the liquor filtered from the silicifluoride of baryta, sulphuric acid is added; it is evaporated to dryness, and the collective quantity of sulphate of strontia and of lime are determined together; the two earths are afterwards separated from each other in the manner indicated (pages 26—403.)



SEPARATION OF SILICATES FROM EACH OTHER WHEN MIXED  
TOGETHER.

Among the non-igneous minerals found in nature some are met with which consist of mixtures of various silicates, such as those called phonolites, aluminous schistus, &c., which minerals produce compounds, some of which may be decomposed by acids, whilst others resist its action. They may be analysed in the following manner:—The substance is reduced into as fine a powder as possible, and allowed to dry at an extremely gentle heat until it ceases to lose weight; after having weighed it, concentrated muriatic acid is poured upon it, and it is left to act upon it at a gentle heat, until the portion which is attackable by acids has been completely decomposed; water is then added, the undissolved portion is allowed to settle well and filtered, the insoluble part is washed. Considering, however, that a portion of this residuum might easily be mechanically carried through the filter during the washing, it is advisable to add a few drops of muriatic acid to the water used for washing, which ordinarily prevents this effect from taking place. The filtrate must, however, be received in another glass than that in which the first filtrate has been received, in order to avoid having too large a quantity of liquid to filter again, should it at first pass turbid.

The undissolved portion consists of the portions of the combinations which have resisted the action of the acid, and of the silicic acid of the portion which was decomposed. The filtered muriatic acid liquor is examined by the means which have been indicated (page 458). The constituents which are separated therefrom represent the composition of the portion of the combination which has been decomposed by the acid, except the silicic acid; I shall only remark here, that it is advisable to treat the muriatic acid liquor by an aqueous solution of sulphuretted hydrogen, because the mixed silicates pretty often contain small quantities of metals, especially protoxyde of copper.

\* The portion which has refused to dissolve is boiled while still moist with a solution of carbonate of soda, which dissolves the silicic acid of the decomposed combination, but does not act upon the portion which was not attacked by the acid. Several precautions, however, must be taken during the solution of the silicic acid. If the totality of that which has not dissolved, is boiled with the alkaline liquor, and the operator proceeds to filter, the silicic acid on cooling separates in a gelatinous form, which stops the filtering. It is therefore necessary to boil only small quantities of the undissolved portion, no more of it being taken at one time with a platinum spoon, than might be held on the point of a knife; it is then thrown into the solution of the alkaline carbonate, boiled therein, and filtered whilst yet warm. The operator continues to do so, until all the undissolved residuum has been boiled with the alkaline liquor. Lastly, the filter and the parcels which may yet adhere to it, are boiled also in the alkaline liquor, and the whole is filtered as above. A little muriatic acid is added to the water used for washing, in order to remove completely all the alkali which might adhere. A platinum capsula is the vessel which answers best for boiling the solution of the alkaline carbonate.

\* The filtered alkaline solution is carefully supersaturated by means of muriatic acid; it is evaporated to dryness with the precautions mentioned (page 463), in order to obtain the silicic acid. After having determined this acid, the operator possesses all the constituents of the portion of the compound which had been decomposed by the acids.

\* The portion of the combination which resisted the action of muriatic acid, and the solution of the alkaline carbonate, is dried. It often contains some carbon, the quantity of which may be determined by the loss which the substance sustains by ignition in the air. The substance is then mixed with carbonate of alkali, or else, if it contains an alkali, with carbonate of

baryta, and the constituents are then determined in the manner which was indicated before. In many cases, this portion of the combination consists of felspar. After having separated the silicic acid in the usual manner, it is advisable also, in this analysis, to add an aqueous solution of sulphuretted hydrogen to the filtered acid liquor, in order to separate small quantities of protoxyde of copper, which it generally contains.

\* It is advisable to take another portion of the combination, and to decompose it immediately by carbonate of alkali, or by carbonate of baryta; the operator may then easily see whether the analysis of the portions which have been decomposed, or left undecomposed by acids, is exact. When the analyst does not wish to make this additional analysis, he must at least determine the quantity of water contained in the portion which is decomposed by acids. By igniting the combination in the air, the water evaporates; but the carbonaceous matter is burnt at the same time, the quantity of which is known by igniting the portion of the substance which has not been decomposed by acids.

## CHAPTER XLV.

## TANTALUM.

## DETERMINATION OF TANTALIC ACID.

THE combinations of tantalic acid found in nature resist the action of muriatic acid, and can be decomposed only by fusion with carbonate of alkali, or hydrate of potash. The result of this operation is a tantalate of alkali; but the whole of this salt does not remain in an insoluble state on treating the fused mass by water, because, when the excess of alkali has been removed, it then begins to dissolve.<sup>1</sup> If the solution of the tantalate of alkali is saturated with muriatic acid, in order to precipitate the tantalic acid,<sup>2</sup> or if the mass fused with alkali is at once treated by water and muriatic acid, it is very difficult to obtain immediately the whole of the tantalic acid. It often happens that other portions have to be separated from other substances, which is attended with difficulties, and renders the result of the analysis uncertain.

Berzelius proposed therefore to decompose the combinations of tantalic acid by means of bisulphate of potash, which method yields much more accurate results. The combination is reduced

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<sup>1</sup> According to Berzelius, tantalate of potash is not even quite insoluble in a solution containing an excess of alkali. The tantalate of soda is much less soluble than the salt of potash.—Ed.

<sup>2</sup> Tantalate of potash and of soda are precipitated from the solutions by all acids, even by carbonic acid.—Ed.

into very fine powder, by levigation, and when the powder is dry, a certain quantity of it is mixed with six or eight times its weight of bisulphate of potash in a large platinum crucible, and the whole is heated by the flame of an argand spirit-lamp, until the fused mass is red hot. As soon as the mass has become like a limpid solution, and no powder is perceived at the bottom of the crucible, it is allowed to cool. The fused mass is then boiled with a large quantity of water until it ceases to dissolve anything. The whole of the tantalic acid which had dissolved in the fused bisulphate of potash remains behind, whilst the bases which were contained in the compound are dissolved by the free sulphuric acid. The tantalic acid is separated by filtering.

SEPARATION OF TANTALIC ACID FROM THE METALLIC OXYDES  
AND FROM THE EARTHS.

Fusion with bisulphate of potash is also the method employed to separate tantalic acid from almost all the substances with which it may be combined. Yet, according to Berzelius, it often happens that the tantalic acid thus separated is not pure, and that it still retains a small quantity of substances which could not be separated from it by fusion with bisulphate of potash. These substances are principally peroxyde of tin, peroxyde of iron, and often also tungstic acid, the quantity of which must be determined.

After having carefully and thoroughly washed the tantalic acid which has remained undissolved, it is digested with hydrosulphuret of ammonia, which dissolves the tungstic acid and peroxyde of tin; the peroxyde of iron is thereby converted into sulphuret of iron, which remains with the tantalic acid, the latter not being acted upon by this reagent. The best manner of conducting this operation is as follows:—

The funnel containing the filter on which the impure tantalic acid has been collected, is put into the neck of a bottle, and the joint is closed with a thick layer of tallow, in order to avoid all egress of or communication with the air. Hydrosulphuret of

ammonia is then poured upon the tantalic acid; the reagent, not being able to flow into the bottle through the filtering paper, remains therefore in contact with the acid for a long time. When the operator believes that the peroxyde of tin and the tungstic acid have been completely converted into metallic sulphurets, and have been dissolved by the hydrosulphuret of ammonia, the liquid in the filter is allowed to percolate. The tantalic acid mixed with sulphuret of iron is washed with water to which a little hydrosulphuret of ammonia has been added, and then, without removing the acid from the funnel, muriatic acid is poured upon it, with which it is left in digestion for some time, as was done before with respect to the hydrosulphuret of ammonia. When the sulphuret of iron has been thus dissolved, the liquor is allowed to percolate, the tantalic acid is washed with boiling water, dried, ignited, and weighed. For greater precision it is advisable, after the weighing, to treat the tantalic acid before the blow-pipe, in order to make sure that it no longer contains any peroxyde of tin nor tungstic acid.

Berzelius generally precipitates the solution in hydrosulphuret of ammonia by nitric acid, and treats the precipitate by aqua regia. The tungstic acid which has not dissolved is then separated by filtering, and washed with acidified water. The peroxyde of tin is precipitated from the solution in aqua regia by ammonia. This method of separating tungstic acid from peroxyde of tin is not perfectly exact, but none better is known (page 308). The muriatic solution of the iron is mixed with the liquor which has been separated from the impure tantalic acid by filtering; the liquid contains afterwards iron and a little tin, for separating which from each other, sulphuretted hydrogen is the best reagent.

Such is the method of analysis to be employed when tantalic acid is combined with only small quantities of bases, such as in the mineral called tantalite. But when the bases are in larger

quantity, as in the mineral called yttro-tantalite,<sup>1</sup> another method is resorted to. The combination is likewise fused with bisulphate of potash, and the fused combination is treated with a sufficient quantity of boiling water. This being done, the liquor is decanted, and the residuum is digested for a long time with concentrated muriatic acid. That which has refused to dissolve is collected on a filter and washed. The muriatic acid solution is mixed with the other liquor. That which has not dissolved is digested with hydrosulphuret of ammonia, and subsequently with muriatic acid, as indicated before. That which remains after these two operations is tantalic acid.

The peroxyde of tin and tungstic acid are precipitated from the acid liquor by sulphuretted hydrogen; the metallic sulphurets thus obtained are then mixed with those which were precipitated

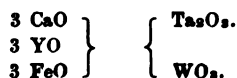
<sup>1</sup> Tantalite is a combination of tantalic acid with protoxyde of iron and of manganese, and is found principally at Kimito in Finland, and Bodennais in Bavaria. A sample of the first, analysed by Berzelius, and one of the second analysed by Vogel, gave the following results:

	KIMITO.	BODENNAIS.
Tantalic Acid . . . .	83.2	75.0
Protoxyde of Iron . . .	7.2	17.0
Protoxyde of Manganese .	7.4	5.0
Oxyde of Tin . . . .	0.6	1.0
Lime . . . . .	Trace.	...
	98.4—Berzelius.	98.0—Vogel.

The three varieties of yttro-tantalite, dark, black, and yellow, described and analysed by Berzelius, vary considerably in composition, and are regarded by that illustrious chemist as a mechanical mixture of tantalum, yttria, uranium, lime, and tungstic acid.

The dark variety from Ytterby is represented by Berzelius as  $(3 \text{ YO} + 3 \text{ CaO}) \text{ Ta}_2 \text{ O}_5$ .

The black variety from Finbo, Ytterby and Kararfvet, as



The yellow variety  $(3 \text{ YO} + \text{U}_2 \text{ O}_3) \text{ Ta}_2 \text{ O}_5$ .

The Yttro-tantalate called Fergusinite from Kikertaurmak, near Cape Farewell in Greenland, contains protoxyde of cerium, and of zirconia; it is represented by Berzelius as  $3 \text{ YO} + \text{Ta}_2 \text{ O}_5, 3 \text{ CeO} + \text{Ta}_2 \text{ O}_5, \text{Zr}_2 \text{ O}_5 + \text{Ta}_2 \text{ O}_5$ .

by means of an acid from the solution in hydrosulphuret of ammonia. By adding a little nitric acid to the liquor filtered from the metallic sulphurets, and heating it, or by passing a current of chlorine through it, the protoxyde of iron is converted into peroxyde of iron, which is then precipitated by ammonia, along with the yttria and peroxyde of uranium, if these two substances are present. The precipitate produced is collected as rapidly as possible upon a filter, and the lime contained in the filtered liquor is precipitated by means of oxalate of ammonia. The precipitated peroxyde of iron, yttria, and peroxyde of uranium are redissolved in nitric acid. In thus redissolving the precipitate a small quantity of tantalic acid is again left undissolved, which small quantity must be determined. The peroxyde of iron is precipitated from the solution by means of carbonate of ammonia. It is more difficult to separate yttria and peroxyde of uranium from each other.

#### SEPARATION OF TANTALIC FROM SILICIC ACID.

When silicic and tantalic acid have to be separated from each other, the following method may be employed:—The mixture is ignited, and treated by hydrofluoric acid in a platinum vessel, by which means the silicic acid is dissolved, whilst the tantalic acid which has been ignited is not soluble in this reagent. It is true that, according to Berzelius, the hydrofluoric acid retains a small quantity of it, but it may be altogether separated by igniting it.

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The French edition has the following remark by Ed. Peligot:—

#### SEPARATION OF TANTALIC FROM TITANIC ACID.

\* These two substances, which are sometimes united in the same mineral, may be separated, according to Wöhler, in the following manner:—



\* These substances are mixed with sugar, the mixture is carbonised and exposed to the action of a current of dry chlorine in a porcelain tube, heated red hot. The chlorides distil over, and are collected in water ; they are then treated by sulphuric acid, which precipitates the tantalic acid, and leaves the titanic acid in solution.

## CHAPTER XLVI.

## CARBON.

## DETERMINATION OF CARBON.

THE quantitative determination of carbon may be effected in various ways. The method to be adopted differs according to the state in which the carbon exists in the substance.

When the carbon is only in the state of mixture with another substance, or if the latter contains it in such a state that it can easily be burnt, it is sometimes sufficient to ignite the substance in contact with the air, and the weight of the carbon is determined from the loss. This method, however, cannot be resorted to when there are other volatile substances, for it is then impossible to determine the quantity of the carbon from the loss sustained. Some chemists have tried to heat such substances in a small retort out of the contact of the air, in order to expel the volatile constituents, the quantity of which was then determined from the loss of weight; the substance was subsequently ignited in contact with the air, in order to burn the carbon, the quantity of which was estimated from the second loss thus sustained. The results obtained by this method, however, are inaccurate, and even in many cases fall considerably short of the truth, because volatile constituents very often form with carbon combinations which are volatile also.

In order to determine the quantity of carbon contained in a substance, especially if volatile bodies are present, the following

method is usually employed:—The carbon is converted into carbonic acid, and the volume of this acid is determined, or else it is passed through lime-water or baryta-water, and the quantity of the carbon is calculated from the weight of the earthy carbonates. In order to convert the carbon into carbonic acid, various methods are employed according to its more or less intimate combination with other substances, or according to the nature of these substances.

The best method of oxydising carbon contained in a substance is that which was first proposed by Gay Lussac; it consists in weighing a certain portion of the substance, and igniting it in a suitable apparatus with a large excess of protoxyde of copper. The carbon reduces the oxyde, whilst, if the latter is in sufficient quantity, the carbon is transformed into carbonic acid. When the substance operated upon contains still certain constituents capable of reducing the protoxyde of copper (*oxyde cuivrique*) other volatile products are usually obtained besides carbonic acid. The substances which contain carbon, and the decomposition of which can be effected by protoxyde of copper (*oxyde cuivrique*) most generally contain hydrogen also, owing to which, during the ignition with the protoxyde of copper, not only carbonic acid, but water also, is produced. The description of the apparatus suited to this operation, and of the precautions which must be observed, will be given in full in Chapter LIII., which will treat of the quantitative determination of hydrogen and of its combinations.

In certain cases, instead of protoxyde of copper (*oxyde cuivrique*) oxygen gas, or chlorate of potash, or even sometimes nitrate of potash, may be employed. The carbon is thereby converted into carbonic acid. When chlorate of potash is used the apparatus is generally similar to that which is adopted for the method by protoxyde of copper. Nitrate of potash is frequently employed, especially for the quantitative analysis of mixtures of carbon with other combustible substances

prepared for technical or manufacturing purposes. In such cases the quantity of the acids produced by the oxydisation of the other substances is generally determined, which acid combines with the potash of the nitrate of potash ; the loss indicates the total amount or quantity of the carbonic acid or of the carbon. Yet it is possible to determine, in a direct manner, the quantity of the carbonic acid which was produced : a portion of this acid combines with the potash to form carbonate of potash, whilst another is disengaged in a free state.

When carbon is combined with substances which are capable of being dissolved by acids which do not exercise an oxydising action—for example, in muriatic acid—it is obtained in the state of an insoluble residuum. This residuum is collected on a weighed filter, washed, and after having dried it thoroughly, its weight is determined. It is difficult to weigh with great accuracy a considerable quantity of charcoal in powder, but for small quantities this is easily done. After having weighed the carbon, the operator must never neglect to burn it in the open air, in order to ascertain whether no foreign substances are left in the state of ashes, the weight of which must be determined and deducted from that of the charcoal. But if the substances combined with the carbon are soluble in dilute muriatic acid under disengagement of hydrogen from the decomposition of the water, this method cannot be employed, because the hydrogen gas liberated forms with carbon compounds which are volatile.

#### SEPARATION OF CARBON FROM SILICIOUS COMPOUNDS.

Carbon is rarely contained in considerable quantity in silicious compounds. The mineral called pyrorthite<sup>1</sup> is one of the small number of native silicious compounds which are in this predicament. Berzelius, who analysed this compound, determined the quantity of the carbon from the loss which a weighed portion of

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<sup>1</sup> Pyrorthite is considered by Berzelius to be a mixture containing about one-third

this mineral sustained by ignition in the air; but as this mineral contains water besides, it is necessary to take another weighed portion, to ignite it in a retort out of the contact of the air, and determine from the loss, the quantity of the water, and other volatile substances.

\* When silicious compounds contain only very small quantities of carbon, which is the case generally with those which contain much magnesia, it is difficult to determine the quantity in an accurate manner. If the operator possessed a tolerably large quantity of the compound, the proportion of the carbon might be attempted by igniting the compound with protoxyde of copper.

#### SEPARATION OF CARBON FROM PHOSPHORUS.

Phosphorus forms with carbon compounds none of which have been as yet accurately analysed. If this body contained carbon, it might be eliminated by igniting the mixture in contact with the air.

#### SEPARATION OF CARBON FROM SULPHUR.

Berzelius and Marcet have analysed the combination of carbon and sulphur by passing the vapours of sulphuret of carbon (*sulfide carbonique*) upon red-hot peroxyde of iron. The result was a production of sulphuret of iron and of carbonic acid gas, which was collected over mercury; but some sulphurous acid gas was formed at the same time, mixed with the carbonic acid.

of its weight of carbon, and one-fourth of water. His analysis of that substance is as follows:—

Protoxyde of Cerium . . . . .	13.92
Silica . . . . .	10.43
Lime . . . . .	1.81
Alumina . . . . .	3.59
Protoxyde of Iron . . . . .	6.08
Protoxyde of Manganese . . . . .	1.39
Yttria . . . . .	4.87
Water . . . . .	26.50
Carbon . . . . .	31.41
	<hr/>
	100.000

The peroxyde of iron had been put in a glass tube, which was kept at a red heat during the whole of the experiment. The vapours of the sulphuret of carbon were passed over it in a very slow and uniform manner. The process was as follows:—The sulphuret of carbon was put in a small retort and weighed therein; the retort was then connected air-tight with the cold portion of the tube. The retort was then heated by means of a lamp placed, not underneath, but by the side of it, and the radiating heat of the flame produced a heat sufficient to cause a single bubble of gas to ascend, about every minute's time, in the bell over the mercury. The retort was sheltered by a sheet-iron screen from the radiating heat of the furnace, in which the glass tube containing the peroxyde of iron was kept at a red heat. The operation being finished, the peroxyde of iron, mostly converted into sulphuret of iron, was carefully treated by aqua regia, and the quantity of sulphuric acid produced and of liberated sulphur were determined. The gases which were collected in the bell over the mercury were separated from each other in the following manner:—A small bottle made of glass tube was filled with a weighed quantity of peroxyde of lead, and closed with a piece of leather glove, and, by means of a piece of annealed iron wire to which it was fixed, it was introduced through the mercury into the glass bell. The sulphurous acid became oxydised by the peroxyde of lead, and formed sulphate of lead. Twelve hours afterwards, a second small bottle, filled with hydrate of potash, was introduced in the same manner into the glass bell, in order to absorb the carbonic acid. When all absorption ceased, and the bell contained nothing else than the atmospheric air which existed in the apparatus before the experiment, the small bottles made of glass tube above-mentioned were weighed, and, from the augmentation of their weight, the quantities of the sulphuric and carbonic acids produced were ascertained, from which the composition of the sulphuret of carbon could subsequently be easily determined.

When, on the contrary, the substance to be quantitatively

analysed is merely a mixture of sulphur and of carbon, the best method consists in weighing a certain quantity of it, and heating it slowly out of the contact of the air; the sulphur volatilises whilst the carbon remains, the weight of the latter is then determined. In order to avoid the access of the air completely the mixture should be heated in an atmosphere of gases which have no action upon carbon. Hydrogen gas answers this purpose best. The experiment is performed in an apparatus similar to that described (page 138).

The mixture is put in the glass bulb *g*, which is then weighed, and the sulphur which is volatilised is expelled completely from the tube by means of a small spirit-lamp. After the complete cooling, the bulb *g* is again weighed, which indicates the quantity of the charcoal.

\* The mixture of sulphur and charcoal may also be analysed by passing a current of dry chlorine gas over it, which chlorine must be free from atmospheric air. When the apparatus is completely filled with chlorine, heat is applied to the mixture, chloride of sulphur distils over, which is collected in a flask half or one-third filled with water (page 212). The whole of the charcoal remains. The chloride of sulphur is converted, by the action of the excess of chlorine, into sulphuric acid, whilst a portion of the sulphur separates. The latter is determined in the state of sulphur, and the sulphuric acid in that of sulphate of baryta.

If the operator wishes to determine the quantity of the sulphur, not from the loss but in an immediate manner, this substance should be converted into sulphuric acid, which is precipitated afterwards by a solution of a salt of baryta. The most convenient method of oxydising the sulphur in a mixture of this body with charcoal consists, according to Gay Lussac, in weighing a certain portion of the mixture, and in mixing it intimately with carbonate of potash or of soda, and then with nitrate of potash and chloride of sodium, and the whole is then exposed to the fire. A platinum crucible may be used for the purpose

without fear of its being attacked. The mass burns quickly and becomes white. The residuum is dissolved in water, the solution is carefully acidified by muriatic acid, and a solution of chloride of barium is then added. The quantity of the sulphur is calculated afterwards from that of the sulphate of baryta produced.

The addition of the alkaline carbonate is necessary in order to prevent the volatilisation of any sulphur; that of the chloride of sodium renders the combustion less violent. The proportions to be employed are, for one part of the mixture of sulphur and carbon, four parts of alkaline carbonate, seven or eight of nitrate of potash, and sixteen of chloride of sodium.<sup>1</sup>

The composition of GUNPOWDER may thus be quantitatively determined in a very easy manner. The quantity of the nitre is found by treating a weighed portion of the powder by water,<sup>2</sup> and evaporating to dryness the liquor separated by filtering from the charcoal and sulphur. In order to determine the quantity of the charcoal, the insoluble residuum is dried with care, and it is weighed upon a weighed filter; and a very accurately weighed portion thereof is now submitted to the treatment which has been just described. Another portion of the gunpowder is then mixed with its own weight of carbonate of alkali, an equal proportion of nitrate of potash, a quadruple weight of chloride of sodium, and the whole is treated as was said above.

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<sup>1</sup> Sulphur and carbon may also be separated from each other by means of sulphite of potash, which dissolves the sulphur, and is thereby converted into hyposulphite of potash, whilst the carbon remains untouched, and may be at once collected on a filter, dried and weighed.—Ed.

<sup>2</sup> The weighed portion, about 50 grains of gunpowder, should be boiled with about eight times its weight of distilled water, by which means the nitrate of potash is dissolved, whilst the sulphur and carbon which are left behind must be thoroughly washed on the filter, until the water of the washing which passes through is found to pass quite pure. The saline mass which remains, after the evaporation of the filtrate, ordinarily contains some chloride of sodium, the amount of which may be determined as chloride of silver. In order to determine the amount of moisture contained in the sample, it should be dried by means of the water bath, or, which is better, in vacuo over sulphuric acid, until it ceases to lose weight.—Ed.



SEPARATION OF CARBON FROM METALS, AND ESPECIALLY  
FROM IRON.

The analysis of the combinations of carbon with metals, often presents very great difficulties. A very small number of such combinations is known; the most important of which are unquestionably those which it forms with iron, the composition of which may often prove of paramount importance in a technical point of view. When carburetted iron is treated by acids which have not an oxydising action, for example, by muriatic acid, a volume of hydrogen gas is obtained, which is less than when a same quantity of pure iron is submitted to a similar treatment. In the first case, a portion of the carbon unites with the hydrogen, with which it forms a volatile oil, and after the iron has dissolved, the residuum is far from containing the whole of the carbon. The quantity of the latter might be estimated from the loss by treating the muriatic acid solution of the carburetted iron by nitric acid, in order to convert the protoxyde into peroxyde of iron, and calculating the quantity of the iron from that of the peroxyde of iron obtained. If, in that case, the solution of the peroxyde of iron, or the residuum undissolved by the acid, contained besides small quantities of protoxyde of manganese, of magnesia, of sulphuric acid, of phosphoric acid, or of silicic acid, these substances might be quantitatively determined either in the liquor, or in the residuum ignited in contact with the air, by the methods which have been described before. These substances exist in the iron in the state of manganese, of magnesium, of sulphur, of phosphorus, and of silicium.

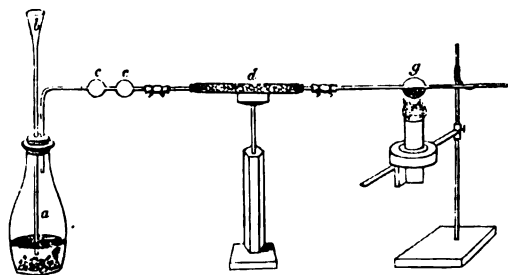
But, as the quantity of carbon is generally very trifling, this method would yield but inaccurate results. The best method, according to Berzelius, is the following:—

Chloride of silver is to be fused into a cake, and introduced into a vessel containing water, and sheltered from the contact of the air by a plate of glass. The piece of carburetted iron

under examination is then deposited upon the chloride of silver. The chloride is reduced by the iron, which is thus converted into protochloride of iron, and dissolved ; the charcoal remains on the cake of partly reduced silver, from which it can be easily separated, and collected upon a weighed filter. The operation is long when the piece of iron is thick. The chloride of silver must be employed in excess, that is to say, about five parts and one-third for one of iron. The contact of the air must be avoided, because hydrate of peroxyde of iron might thus be separated from the solution of the protochloride, and mix with the charcoal. This accident needs not be apprehended when a few drops of muriatic acid are added ; this precaution besides is advantageous, inasmuch as the operation proceeds then more rapidly ; yet it is necessary to take care that the acid added is in too small proportion to have a dissolving action upon the iron.

\* This method may be applied to other methods besides iron, provided they be capable of reducing the silver of the chloride of that metal, and the foreign substances with which they are mixed may be thus qualitatively and quantitatively determined.

Another method proposed also by Berzelius, consists in treating a weighed quantity of carburetted iron by dry chlorine gas, in an apparatus similar to that represented (page 128). The iron



is heated to redness, and the operator endeavours to sublime the perchloride of iron formed, and to expel it from the bulb. The residuum consists of carbon, the weight of which may be deter-

mined. It is necessary to take care that the chlorine which is passed through the bulb contains no oxygen or atmospheric air, because some carbon might then be volatilised in the state of carbonic acid or of oxyde of carbon.

As, however, it is often very difficult to obtain chlorine in a perfectly pure state, bromine might perhaps be advantageously substituted. In that case a certain portion of the carburetted iron to be examined being weighed, is put into a glass, water is poured upon it, and bromine is then added. The result would be bromide of iron, and charcoal would remain. It should then be separated from the liquor by filtering, and dried upon a weighed filter; but in this experiment it would be necessary to pulverise the iron, or, at any rate, to reduce it into small bits.

\* Iodine might also be used instead of chlorine and bromine, with the same precautions as mentioned for bromine.

Berzelius again proposed *another method*, which consists in heating the carburetted iron to redness, and passing over it a slow current of oxygen gas. The iron is thereby transformed into ferroso-ferric oxyde, and the charcoal into carbonic acid, which is received into lime or baryta-water until the liquor ceases to become turbid. The quantity of the carbon is afterwards calculated from that of the earthy carbonate obtained.

\* A *fourth method*, proposed likewise by Berzelius for the determination of the carbon in a carburetted iron, is the following:—The iron is first, if possible, converted into iron-filings, water is poured upon it, and nitric acid, perfectly free from muriatic and from nitrous acids, is gradually added by small portions at a time. The respective quantities of the water and of the acid employed are of no consequence, yet the experiment proceeds better when that of the water is not too large. The mixture becomes hot, and may, without inconvenience, reach + 50° cent. The solution proceeds then

more rapidly. As soon as the acid is saturated the solution, however diligently stirred, begins to cool, when a fresh portion of acid is added. When the liquor is sufficiently concentrated, it is decanted, and the residuum is treated by a fresh portion of nitric acid and of water. It is important, however, that the iron filings should not remain too long, for example, five or six hours, in contact with the saturated solution, for the result would then be a cohesive blue mass upon which the fresh portion of acid added would act but slowly. During the experiment the acid becomes yellowish and turbid, and the liquor, in the midst of which charcoal in a state of fine division is swimming, becomes of a pale grey colour. No gas is disengaged during the operation. Nitrate of ammonia and nitrate of protoxyde of iron are formed, whilst the carbon remains, as well as other foreign alloys which existed in the iron, and also the silicic acid, if silicium was present. The solution goes on rapidly, when the filings are constantly stirred; when finished it may be heated to ebullition without producing any peroxyde of iron, or disengaging nitric oxyde. After having separated the insoluble substances from the solution, the latter is boiled with nitric acid, in order to convert the protoxyde of iron into peroxyde of iron.

\* Besides these methods Berthier proposed *another process* by which the quantity of the carbon contained in the iron may be accurately determined, even when the iron contains silicium, in which case, according to this chemist, a less quantity of carbon is obtained than should be when the analysis is made by means of chlorine, of bromine, or of iodine. This method consists in oxydising the iron by the oxygen of the atmospheric air at the ordinary temperature. This is done by keeping it constantly in a moist state, and dissolving in muriatic acid the oxyde which has thus formed; the carbon and silicic acid remain in an insoluble state. When operating upon moderate quantities and in capacious vessels, there is no sensible elevation of temperature, nor disengagement of hydrogen gas, so that the iron and the silicium are oxydised at the expense of the

atmospheric air alone, and not of the water. Experience has taught that this method yields larger quantities of carbon from iron than any other.

\* The experiment requires eight days when operating upon nine or ten grammes of carburetted iron, but it goes on more rapidly in proportion as the iron is in a greater state of division. When the iron is very brittle, such as white cast-iron, or hardened steel, it may be broken in a cast-iron mortar, sifted, and triturated in an agate mortar. If, on the contrary, it is more or less malleable, as in grey cast-iron, it is filed, but the files used for this purpose must be very hard and fine. About ten grammes of these filings are then placed in a large porcelain capsula, moistened with water, and the whole is left at rest. The next morning the iron is found covered with a large quantity of rust; it is moistened again, and triturated, water is added, and the peroxyde of iron produced is separated by levigation; the portion of the metal which has not been oxydised is left again in the moist state, taking care to keep it so. When the oxydisation is finished, an excess of muriatic acid is added to all the liquors and to the deposit of peroxyde of iron; the whole is evaporated to dryness; the residuum is treated by muriatic acid, and washed. It is advisable, after the drying, to heat it out of the contact of the air, and then to weigh it. It is afterwards ignited in a small platinum crucible in contact with the air, until all the carbon has been burnt away, and the residuum is weighed; the loss indicates the quantity of the carbon. The residuum ultimately found is silicic acid, and, if it contains spangles of graphite, it should be boiled with a solution of potash, which dissolves the silicic acid, and leaves the graphite.

\* A very small portion of acid accelerates much the oxydisation of the iron left exposed to the air, but as a little disengagement of hydrogen may thus take place, a small loss of carbon is sustained; this addition should not, therefore, be made, but a small portion of chloride of sodium may very well be added to the

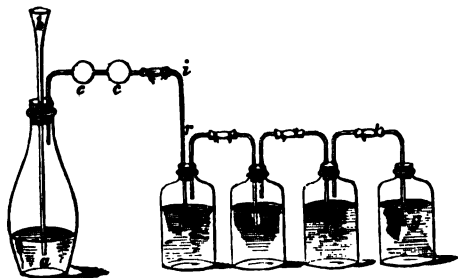
water used for moistening the iron, by which means the oxydisation is hastened without producing the slightest disengagement of hydrogen.

\* Whenever carbon has to be quantitatively determined in iron, it is absolutely necessary to know in what state it is contained in it. In grey cast-iron, part of the carbon, according to Karsten, is chemically combined with the iron in the state of carburet of iron, whilst another portion is only mixed with it in the state of pure crystalline carbon or graphite. The latter substance was formerly looked upon as a chemical combination of a small quantity of iron with a great deal of carbon, but it has been ascertained since, according to Karsten, that this mineral consists only of pure carbon. Karsten indicated the following method of determining the quantity of the graphite contained in cast-iron. A certain quantity of cast-iron is weighed and dissolved in nitric acid, to which a little muriatic acid has been added; the residuum consists of crystalline carbon (graphite), and a combination of carbon produced by the carbon of the carburet of iron having the appearance of an extract; the residuum contains also silicic acid and a few oxydes, the metals of which were combined with the iron. A solution of pure potash is poured upon the residuum, in order to dissolve the extractive compound, and the silicic acid if present, whilst the graphite remains untouched. The latter is washed, and again treated by muriatic acid, in order to obtain it quite pure, after which it is dried, and weighed.

The whole quantity of the carbon is determined in another portion of the cast-iron by means of chloride of silver, and by subtracting that of the graphite obtained in the other experiment, the operator may then know how much carbon was combined with the iron in the state of carburet. He must bear in mind, however, that the carbon liberated by chloride of silver, may still contain silicic acid and other substances, the quantity of which must be determined and deducted from that of the carbon.

As the quantity of the other substances is much less than that of the carbon in carburetted iron, and as it may often be of the highest importance to know exactly to what amount they are contained in it, it is advisable to ascertain the respective quantities of each of them by a separate analysis.

The quantity of sulphur is so inconsiderable, according to Karsten, even in the most brittle iron, that after having oxydised it, by means of aqua regia, it cannot be accurately estimated by means of solution of baryta salts. In order to determine the quantity of sulphur, it is therefore better to dissolve the iron in muriatic acid, and to volatilise all the sulphur which it may contain in the state of sulphuretted hydrogen. To perform this analysis, the operator takes five grammes of the iron in question, reduced into small pieces of the size of millet seed; the metal is dissolved slowly, and without applying heat, in an apparatus similar to that which has been described (page 386).



The bottles contain a metallic solution, for which purpose a solution of protochloride of copper (*chlorure cuivrique*) is preferable. If the operator manages the experiment so that the sulphuretted hydrogen is disengaged extremely slowly, its decomposition is already completed in the first bottle, so that it is not necessary to use more than two of them. The analysis of cast-iron by this method requires from ten to fourteen days; steel, eight or ten days; and bar-iron three or four days for their complete solution. In order that the sulphuretted

hydrogen which remains in the disengagement flask when the solution is finished, may be absorbed by the metallic solution in the bottles, it is driven into them by means of carbonic acid gas, in the manner which was described (page 387).

In order to determine the quantity of PHOSPHORUS contained in carburetted iron, a fresh quantity thereof is dissolved in nitric acid, with the help of heat, by which means the phosphorus is converted into phosphoric acid. Instead of nitric acid, aqua regia may be employed to dissolve the iron, but nitric acid is preferable. The analysis may be performed upon three grammes of iron. The solution is evaporated to dryness in a porcelain capsula, and heated therein as strongly as possible. The dry mass is then mixed in a platinum crucible, with three or four times its weight of carbonate of potash, and the whole is ignited. After cooling, the mass is treated by water, which dissolves the phosphate of potash produced, and the excess of carbonate of potash employed; the residuum consists of peroxyde of iron, which is collected upon a filter. If the iron, which was submitted to analysis, contains sulphur, it is found in the state of sulphate of alkali in the liquor filtered from the peroxyde of iron. When it contains manganese, the solution contains manganate of potash; but this salt is decomposed by a long digestion, and the result is a production of brown flock of sesquioxyde of manganese. The filtered liquor is moderately supersaturated by pouring nitric acid into it, and evaporated to dryness, in order to separate the silicic acid, supposing this substance to have been present. The dry mass is moistened with nitric acid, and after some time, water is poured upon it, which leaves the silicic acid in an insoluble state. Ammonia is then added to the solution, which, if the iron contained any aluminium, produces a precipitate of basic phosphate of alumina. The alkaline liquor is then very slightly acidified by means of acetic acid, and the phosphoric acid is precipitated by means of a solution of acetate of lead. The phosphate of lead thus produced is treated as was said (page 430).



The operator must not forget that, if the iron submitted to analysis contains any sulphur, sulphate of lead may be precipitated along with the phosphate of that oxyde ; but as, in such a case, the quantity of the sulphur has been already determined by another experiment, it is easy to calculate how much sulphate of lead is thus precipitated, which must then be deducted from the quantity of the phosphate of lead obtained. By determining the quantity of the protoxyde of lead, the operator learns how much of this oxyde was combined with the sulphuric acid, and how much with the phosphoric acid.

This method of determining the small quantity of phosphorus in iron, or rather of phosphoric acid in the nitric acid solution, is preferable to that which consists in supersaturating the solution with ammonia, and separating the phosphoric acid by hydrosulphuret of ammonia.

When the latter method is employed, a very small quantity of phosphoric acid may be very easily overlooked, should the whole not have been digested in the hydrosulphuret of ammonia for a sufficient length of time.

If the carburetted iron contains CHROMIUM the quantity of the latter substance may be determined in the same manner as that of phosphorus. By ignition with carbonate of potash, chromate of potash is produced, which, like phosphate of that base, dissolves in water. The remainder of the process is the same ; chromate of lead is produced, and if phosphorus is present at the same time, phosphate of lead is likewise produced, to which the chromate imparts a yellowish tinge. After weighing, the precipitate is treated by muriatic acid and alcohol ; the oxyde of chromium dissolves, and an insoluble residuum of phosphate and of chloride of lead is obtained, which is collected on a filter, and the oxyde of chromium is precipitated from the filtered liquor, by pouring ammonia into it, previously heating it, in order to volatilise the alcohol.

\* If the iron contains VANADIUM, it is first divided into small pieces and fused, according to Sefström, with nitre, and the fused mass is treated by water, which dissolves the vanadate of potash formed. When the liquor has become neutral, the vanadic acid is precipitated by acetate or by nitrate of lead; the precipitate is collected on a filter and washed. Generally it contains phosphoric acid, also some alumina and zirconia. Concentrated muriatic acid is poured upon it, and a little alcohol is added. The mixture is then exposed for some hours to a temperature very near the boiling point. The blue solution of the chloride of vanadium and of the other substances is evaporated to dryness; the residuum is dissolved in water, nitric acid is added, in order to convert the deutoxyde of vanadium into vanadic acid which is then saturated with carbonate of alkali; the solution is evaporated to dryness, the saline mass is ignited in a platinum crucible until quite fused; it is afterwards dissolved in as small a quantity of water as possible, and a piece of muriate of ammonia is plunged in the liquor. As the latter salt gradually dissolves, vanadate of ammonia is formed and falls down, it is collected on a filter and washed with a solution of sal-ammoniac, in order to remove the phosphoric acid, and the sal-ammoniac is extracted by means of alcohol. The vanadate of ammonia is afterwards converted by ignition into vanadic acid, the weight of which is determined.

\* The silicium contained in the iron must be looked for, in the state of silicic acid, both in the insoluble residuum and in the acid solution.

\* When TITANIUM is present, it is always in extremely small proportion, because this metal does not appear capable of forming an alloy with iron, and could be separated only by treating the nitric acid solution, as was said (page 514).

Lastly, in order to determine the quantity of MANGANESE contained in iron, the solution of the metal is treated as was said

(page 93). But in presence of such a large proportion of peroxyde of iron in the liquor it is not difficult to determine even a slight quantity of manganese.

\* The MAGNESIUM which may be contained in the iron is determined in the usual way in the state of magnesia.

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The following remark by M. E. Peligot is in the French edition :—

\* “ M. Fuchs has indicated a method of determining the quantity of the carbon contained in iron, which consists in treating this metal, steel or cast-iron, by a solution of perchloride of iron, the excess of acid of which has been previously saturated with marble. The iron dissolves, and the perchloride of iron is converted into protochloride of iron; a sediment consisting of peroxyde of iron, mixed with charcoal, is at the same time precipitated, which must be treated separately by muriatic acid. This method is a modification of that of Berzelius, which consists in treating the carbonaceous iron by protochloride of copper (*chlorure cuivrique*). The advantage of this method, according to Berzelius, is that the operation can be more readily followed and that it produces peroxyde of iron which is perhaps more easy to separate from the charcoal than copper.

\* “ M. Regnault proposed *another method* for the easy and accurate determination of the carbon contained in cast-iron. Five grammes of cast-iron reduced into filings, when it is soft, or pulverised into a mortar when it is brittle, are mixed with 60 or 80 grammes of chromate of lead, previously fused, one-third or one-fourth of which mixture is set aside. Five grammes of chlorate of potash are then added to the remainder, which chlorate of potash contains about the quantity of oxygen necessary to convert the iron into peroxyde; and the mixture

is introduced into a glass tube, similar to those employed in organic analysis, but which may be much shorter. The portion of the mixture of cast-iron and of chromate of lead, which was set aside, is now added and put over the other portion in the tube, and lastly, an exsiccating apparatus, and a Liebig's apparatus for condensing carbonic acid is adapted to the tube as for performing an organic analysis. The portion of the tube which contains the mixture without chlorate, is brought to a red heat, and when this is done, the operator begins to heat the portion which contains the other mixture with the chlorate, and the heat is gradually advanced in proportion as the disengagement of the gas becomes slower. By operating thus, the cast-iron is first burnt almost completely by the oxygen of the chlorate, and only a very small quantity of this gas escapes from the tube. The temperature then becoming higher, the combustion is finished by the chromate of lead which in fusing oxydises the last portion of the cast-iron. It is advisable to wrap the glass tube in a sheet of copper, because, towards the end, the heat must be strong enough to fuse the chromate of lead completely.

\* "The oxydisation of the cast-iron is complete, which may be ascertained by trituration the mass contained in the tube after the combustion, when it will be seen that not a particle remains capable of being attracted by a magnet. The analysis is besides so easily performed, that it may be completed in less than half an hour.

\* "When the cast-iron contains sulphur, the latter remains altogether in the tube in the state of sulphate of lead."

#### DETERMINATION OF OXYDE OF CARBON.

Oxyde of carbon has rarely to be analysed. In order to determine its quantity it is converted by detonation with oxygen gas into carbonic acid gas from the bulk or weight of which that of the oxyde of carbon is calculated. A sufficient quantity

of carbonic oxyde gas is introduced over the mercurial trough into a graduated tube, disposed in such a way as to be afterwards detonated by the electric spark, and its volume is accurately noted; rather more than half its bulk of oxygen gas is then added, and an electric spark is passed through the mixture. If the carbonic oxyde gas was very pure, one volume of this gas produces one volume of carbonic acid, consequently, if to one volume of carbonic oxyde gas, exactly one-half volume of oxygen gas be added, there must remain exactly one volume of gas after detonation. But in order to ascertain with more precision the quantity of the carbonic acid gas produced, the operator first determines the bulk of the gas after the detonation, and he, then, introduces into it, through the mercury, a small stick of hydrate of potash, very slightly moistened previously, and fixed to the end of a thin iron wire, for example, a piece of annealed pianoforte wire. The carbonic acid gas is absorbed by the potash, and as the mercury gradually ascends into the tube by reason of this absorption, the iron wire is pushed farther up in order that the potash may always be maintained above the mercury. When the absorption has ceased, the alkali is withdrawn with the iron wire, and the bulk of the gas, which remains is accurately determined. In this manner, the precise volume of the carbonic acid gas becomes known, from which the quantity of the oxyde of carbon may then be easily determined. The gas which remains consists, if the oxyde of carbon was pure, of oxygen gas, an excess of which should always be used. The precautions to be observed in this experiment are the same as those which must be taken in general in the quantitative determination of gases, and which will be explained fully in Chapter LIII.

#### DETERMINATION OF OXALIC ACID.

The best method of determining quantitatively the second degree of oxydisation of carbon, namely, oxalic acid, consists in precipitating it in the state of oxalate of lime, by means of the

solution of a salt of lime. Wherefore, when oxalic acid exists in solution in a liquor, it (the liquor) must be first saturated as exactly as possible by means of ammonia, and diluted with water. A solution of a neutral salt of lime is then added ; in most cases that of chloride of calcium is preferable ; the precipitate of oxalate of lime thus produced is washed. The quantity of oxalic acid could be ascertained from the weight of the oxalate of lime, but as it is difficult to expel the water from oxalate of lime by drying, and as it is consequently unsafe to determine this salt with its water, it is best to ignite it, in order to convert it into carbonate of lime, from the weight of which, that of the oxalic acid is determined. The conversion of oxalate into carbonate of lime is effected, as was said (page 25). The operator must take care, in precipitating the oxalate of lime, that the liquor contains no free ammonia, because, by exposure to the air, a precipitate of carbonate of lime would fall down along with the oxalate of lime.

The determination of oxalic acid in the oxalates which are soluble in water, is performed in the same manner. If the oxalate to be examined is a neutral oxalate, it is sufficient to dissolve it in water, and to precipitate it by means of a neutral salt of calcium. If it is an acid oxalate, the solution should first be exactly saturated with ammonia.

As the neutral oxalates of potash and of soda, and likewise the oxalates of baryta, of strontia, and even of lime, are converted by ignition into neutral carbonates, it is very easy to determine the quantity of the oxalic acid. It is sufficient in effect to weigh a certain portion, to ignite it, and to determine the quantity of the carbonate which has been produced ; that of the oxalic acid, and of the water of crystallisation, is afterwards very easily calculated.

\* Other oxalates cannot be thus analysed. Some of them disengage, whilst being ignited, a mixture of carbonic oxyde,

and of carbonic acid, and leave the base in a pure state; others yield carbonic acid only, the base being reduced, and remaining in the state of metal. These decompositions are not, however, so complete but that the quantity of the oxalic acid can be accurately determined from that of the carbonic acid obtained.

When an insoluble, or sparingly soluble oxalate contains water, and the operator wishes to determine immediately the quantity of the oxalic acid, he may, in most cases, decompose the oxalate by boiling it for a sufficient length of time in a solution of carbonate of potash. If the base forms with carbonic acid an insoluble combination, this combination remains undissolved, whilst the oxalic acid combines with the potash, and is dissolved. The solution is exactly saturated with muriatic acid, and the oxalic acid is precipitated by means of the solution of a neutral salt of lime.

As the oxalic acid of all the oxalates is decomposed by sulphuric acid into a mixture of equal volumes of carbonic oxyde, and of carbonic acid, this solution may be employed as a means of determining accurately the quantity of this acid in all its combinations. A known weight of the oxalate is put into a small flask or in a test tube, closed by a cork traversed by a small bent tube. An excess of concentrated sulphuric acid is poured upon it, and the tube or small flask is immediately closed, and the bent tube is plunged under mercury, so as to open under a graduated tube full of mercury. The small flask or test tube is then heated, at first slowly, in order that when the gas begins to be disengaged, the frothy liquid should not ascend into the tube; the heat is then increased until a little of the sulphuric acid begins to volatilise, and to pass into the graduated tube. The apparatus is then allowed to cool completely, in consequence of which, the mercury gradually ascends through the tube into the small flask; after the cooling is complete, which may be accelerated by wetting the extremity of

the flask with a little ether, the whole capacity of the flask and of the tube, are filled with mercury and with the residuary sulphuric acid, or else a few insignificant bubbles of gas only are left, which the vapours of sulphuric acid have not expelled, and driven into the graduated tube.

\* The quantity of the carbonic acid in the graduated tube is determined in the manner which will be indicated farther on, when speaking of the determination of this acid. From the quantity of the carbonic acid obtained, that of the oxalic acid is calculated by means of the tables.

\* It may be admitted that in determining the volume of the carbonic acid, this gas is dry, the moisture having been absorbed by the sulphuric acid.

#### DETERMINATION OF CARBONIC ACID.

The determination of the third degree of oxydisation of carbon is of frequent occurrence, and may be effected in various ways. When carbonic acid is in the gaseous state, and its quantity has to be determined, the bulk or volume of the gas is first accurately measured in a graduated tube over mercury; a stick of hydrate of potash, slightly moistened, is then introduced through the mercury, by means of an annealed iron wire. The carbonic acid is absorbed by the potash, and as soon as all absorption has ceased, that is about twenty-four hours afterwards, the iron wire and the potash attached thereto is withdrawn, and the volume of the gas which has not been absorbed is accurately determined, by which the volume of the carbonic acid becomes known. From the volume of this gas its weight may then be determined by means of the methods which are indicated at the end of this volume.

If the carbonic acid is contained in a large glass bell, not graduated, standing over mercury, a little hydrate of potash is



introduced into a small tube closed with a piece of kid glove, and after weighing it exactly, it is introduced through the mercury into the glass bell by means of a piece of annealed iron wire. When all absorption has ceased, which will require a certain length of time, the tube containing the hydrate of potash is withdrawn with the iron wire from the glass bell. All the small globules of mercury which may be adhering to it, are carefully removed, and it is weighed. The increase of weight indicates the quantity of the carbonic acid absorbed.

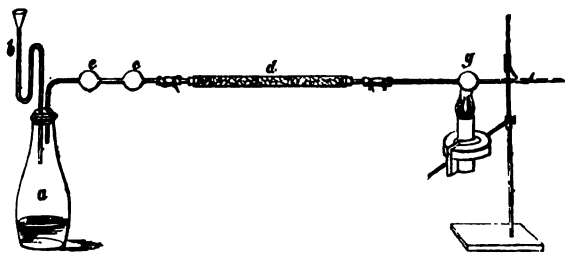
\* It may be easily conceived that this method cannot be employed when the carbonic acid is mixed with gases which can be absorbed by hydrate of potash.

When carbonic acid is contained in solid substances, the method employed to determine it quantitatively varies ordinarily according as it is easy or difficult to separate it by ignition from the bases with which it is combined. Most carbonates lose the whole of their carbonic acid when ignited over an argand spirit-lamp. It is, therefore, very easy to determine the quantity of the carbonic acid which they contain from the loss, provided always that the compound does not contain other volatile substances. This method may be employed for the analyses of all the metallic carbonates properly so called, and for carbonate of magnesia. The metallic oxide or the magnesia remains behind in a pure state. When the oxide is one which is easily reducible, as for example, protoxide of lead, oxide of cadmium, &c., the ignition may be performed in a small counter-poised porcelain crucible. If the reverse is the case, one of platinum is employed.

Some carbonates, indeed, lose their carbonic acid by exposure to a red heat, but their bases are converted into a higher degree of oxydisation during the operation; such are, for example, the carbonates of protoxide of iron, of protoxide of manganese, of oxide of cobalt, which must be analysed by another method

They may be ignited in the atmosphere of a gas which should not permit the oxyde to pass to a higher degree of oxydisement. Among such gases, which can be easily procured, nitrogen and carbonic acid are the only gases which will answer the purpose, the others having a reducing action upon the oxydes with which they thus form other combinations. As an inconvenient apparatus would be required to pass a stream of nitrogen over the weighed compound whilst exposed to a red heat, an atmosphere of carbonic acid is used in preference, although carbonic acid is less easily expelled from its combinations in such an atmosphere than in that of any other gas.

The apparatus employed for this experiment is similar to that described (page 138).



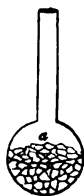
The substance to be analysed is weighed in the glass bulb *g*, which is connected with a disengagement flask containing a mixture of chalk and of dilute nitric acid, or else of dilute sulphuric acid, which produces a disengagement of carbonic acid which is dried by passing it through a tube full of chloride of calcium. When the whole apparatus is filled with carbonic acid, the bulb is slightly ignited by means of an argand spirit-lamp, and kept at a red heat for a pretty long time. After cooling, the stream of carbonic acid being continued all the time, the combination in the glass bulb is weighed. The loss of weight indicates the quantity of the carbonic acid which was contained in the compound operated upon. It is necessary, after the weighing, to connect the bulb again with the apparatus, and to ignite it a second time in order to see whether all the

carbonic acid of the compound has really been expelled, or whether, upon being weighed again, it will still show a loss. Lastly, a little water must be poured upon the ignited compound, and then a little muriatic acid, in order to ascertain that no disengagement of carbonic acid will be produced.

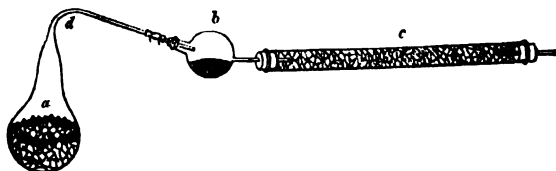
Walmstedt was the first who employed this method, which is used also when the oxydes mentioned above are accompanied by other bases, which is almost always the case, for it is rare to meet with them alone in combination with carbonic acid. The only case in which this method is not applicable is that in which carbonate of lime forms one of the constituents of the compound to be analysed, because ignition by means of an argand spirit-lamp is not adequate to the complete expulsion of the carbonic acid from this salt.

When a carbonate which loses easily its carbonic acid by ignition contains water besides, the quantity of the latter must, of necessity, be determined. To effect this the compound is first ignited in a small retort previously weighed in the empty state, and weighed again, after the introduction of the salt into it, and the water which passes over is collected and weighed. The weight of this water is then deducted from the total loss which the carbonate has sustained after the ignition and the real quantity of the carbonic acid is thus determined.

The best mode of operating is as follows:—The operator takes a tube of strong glass, and a bulb is blown at one of its extremities, so as to produce a small flask, similar to that in the figure below.



The weight of this flask is first noted, and the quantity of the substance intended for analysis is then introduced into it. The whole is then weighed, and the real quantity of carbonate which will be operated upon is thus ascertained. The neck of the flask is then drawn out, at about half an inch from the bulb, and bent, so as to give it the form of a small retort, *a*; the



flask is again weighed, and connected by a tube of caoutchouc with a small receiver, *b*, the point of which penetrates into a small glass tube, *c*, filled with chloride of calcium. The receiver *b*, and the tube *c*, are weighed with the tube of caoutchouc, before the experiment. The apparatus being ready, the bulb of the flask *a*, is heated for a long time by means of a spirit-lamp. The greatest part of the water which is disengaged is collected in the receiver *b*, portion of which water, however, is carried farther in the form of vapour, and is completely absorbed by the chloride of calcium of the tube *c*. The bulb of the flask, *a*, must be made of very strong glass, for it could not otherwise bear the temperature which is necessary for the complete expulsion of the carbonic acid. After complete cooling, the extremity of the retort is cut at *d*, because a drop of water is adhering to the end of the drawn-out point, and this portion, with the receiver *b*, and the tube *c*, are weighed together. Before doing this, however, the operator waits until the carbonic acid gas, which is heavier than the atmospheric air, has been displaced by the latter, the end of the tube cut at *d* is then dried and weighed by itself. The increase of the weight of the receiver *b*, and of the tube *c*, consists of water, deducting, of course, the weight of the tube cut at *d*. The retort, *a*, is now weighed, and to this weight that of the tube

cut in *d*, is added. The loss of weight indicates the collective quantity of water and of carbonic acid, but as that of the water has already been ascertained, it is to be deducted, and the remainder is the weight of the carbonic acid.

As the carbonates which contain water part with it *in toto* more easily than with their carbonic acid, by the action of a moderate heat, and as often a very strong heat is inefficient to expel the carbonic acid completely, it is better to employ the method which has been just described, only for the determination of the water. In order to obtain afterwards the collective quantity of the water, and of the carbonic acid, a certain quantity of the combination is to be weighed and ignited in a platinum crucible. The quantity of the carbonic acid alone may likewise be determined by means which will be described farther on.

Carbonic acid cannot be expelled by ignition from its combinations with the fixed alkalis, baryta, strontia, and even lime; the latter does not lose its carbonic acid even by strong ignition in a platinum crucible, over an argand spirit-lamp. In order to determine the quantity of carbonic acid contained in such combinations, the action of stronger acids must be resorted to, which method is applicable likewise to all the other carbonates.

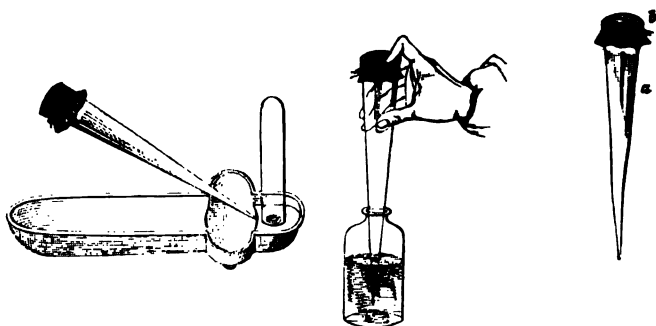
This may be done in various ways. If the quantity of carbonic acid has to be estimated in a solid carbonate, a given weight of the latter is introduced into a glass tube filled with mercury, and placed over the mercurial trough. If the carbonate is in powder, a given weight thereof is wrapped up into thin filtering paper, which is likewise introduced into a graduated tube filled with mercury. A liquid acid is then passed through the mercury into this tube, which acid immediately decomposes the carbonate, and expels its carbonic acid. Muriatic acid of a moderate strength is generally used in preference and in excess. The acid is put in a small tube which can be closed with the thumb when full; thus closed it is plunged through the

mercury under the graduated tube, and the thumb being removed the acid immediately runs through the mercury.<sup>1</sup> A little carbonate of soda must be previously dissolved in the acid in order to saturate it with carbonic acid, that it may not absorb any portion of the carbonic acid which will be disengaged from the combination. When the decomposition of the compound is complete, which is known when the quantity of the carbonic acid produced no longer augments, its volume is determined by means of the methods which will be indicated at the end of this volume.

A *second method* of determining carbonic acid in carbonates consists in decomposing a known weight of the latter by a weighed quantity of acid, and after complete decomposition to calculate from the loss of weight how much carbonic acid has been disengaged.

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<sup>1</sup> This method of introducing the acid is inconvenient, and requires besides a more considerable quantity of mercury than is otherwise requisite. The method which I employ is the following :—

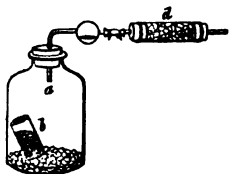


*a* is a glass pipette, having the form of a long funnel, the upper part of which, at *b*, is tied over with a flat piece of sulphurised caoutchouc. The operator introduces the point of the tube into the bottle containing the acid, and pressing the sulphurised caoutchouc at *b* with the finger, the air of the tube is pushed out, and on withdrawing the finger, the acid ascends into the pipette. The pipette being now filled, or partly filled with acid, its pointed extremity is brought through the mercury under the graduated tube, and by pressing the finger on the sulphurised caoutchouc, the acid contents are forced out, and ascend into the graduated tube.—Ed.

In order to determine the quantity of the carbonic acid by the above process, it is sufficient to employ a balance which, when somewhat heavily laden, is still sensible to very small weights; a sufficient quantity of the acid intended to be used for decomposing the compound is then weighed in a vessel, and a weighed quantity of the carbonate to be analysed is added thereto. The vessel must be covered with a concave glass, in order to prevent any loss from taking place by projection from the effervescence produced, and the loss in weight indicates the quantity of the carbonic acid.

This method, however, does not yield a very accurate result; as a long time elapses before the decomposition is completed, it may very easily happen that a little of the acid employed is volatilised, or if not of a very volatile nature, but diluted, that a small quantity of water will evaporate. The loss which results from this is stronger still when a gentle heat is employed to effect the decomposition, which is sometimes the case. Wherefore this method is but seldom employed, except for the purpose of determining the carbonic acid of a compound, as follows:—The compound is weighed, and also the acid to be employed, and one of the liquors is then carefully added to the other; the loss of weight indicates the quantity of the carbonic acid, but a long time is required. For technical purposes this method is often very suitable.

In order to avoid all loss, which is absolutely necessary for scientific purposes, the experiment should be performed as follows:—



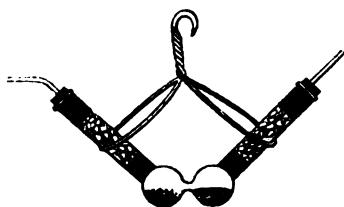
The operator takes a bottle, *a*, which has a somewhat large mouth, but which is capable of being closed by a cork, and a

weighed quantity of the carbonate to be analysed is introduced into it; a small vessel, *b*, (which is best made of a barometer tube closed at one end), containing muriatic or some other acid, in sufficient quantity to effect the decomposition of the substance, is introduced also into the bottle, *a*, taking care, however, that the acid does not come in contact with the substance submitted to analysis, which is effected by putting the vessel, *b*, above spoken of, and containing the acid, in an upright position, and leaning against the side of bottle, *a*, which is then to be closed with a cork through which a disengagement tube passes, connected by a tube of indian rubber to another tube filled with [fused] chloride of calcium. The whole is then weighed with a balance capable of indicating small weights, even when heavily laden. This being done, the apparatus is shaken, so as to upset the small vessel or tube, *b*, containing the acid, which, coming in contact with the carbonate, effects its decomposition. All the water which in other apparatuses would be lost by projection or by evaporation, is absorbed by the chloride of calcium of the tube *d*. If the carbonate is of difficult decomposition, or cannot be decomposed except with the help of heat, the bottle may be heated without fear of loss. As soon as the decomposition is completed, the bottle is uncorked and left open for some time, in order that the carbonic acid which it contains may mix with the atmospheric air, and be expelled by it. The cork is then replaced on the bottle and the weight is determined, but not until the ensuing day. The loss of weight indicates the quantity of carbonic acid which has disengaged.

Fritsche employed for the determination of carbonic acid a very convenient apparatus, which is represented in the following figure, reduced to the fourth of its real size, which supersedes the necessity of describing it more fully. The double noose with the hook is made of platinum wire, and serves to suspend the apparatus to the beam of the balance, which tries it less, the weight being thus much reduced. The apparatus is first weighed empty, and then weighed again after the introduction of the



compound to be analysed and previously reduced to powder. The pulverised compound is introduced into one of the bulbs of the apparatus by means of a platinum spoon, and the whole is



weighed again, as was said. The acid is then carefully poured in the other bulb by means of a long funnel, and the two tubes are then filled with pieces of chloride of calcium, after having previously put some cotton at the bottom of the tube towards the bulbs, and the two corks, each provided with a small tube, are put on. The whole apparatus is then weighed again, the weight of which does not exceed twenty-five grammes at most, and the acid is then carefully made to flow over the carbonate in the other bulb. When the disengagement of the carbonic acid has ceased, the liquor is heated in order to expel completely the carbonic acid which it might contain; the apparatus is allowed to cool, and after having connected a second tube filled with chloride of calcium with one of the tubes, the operator blows out, with dry lips, all the carbonic acid contained in the apparatus. The loss of weight indicates exactly the quantity of carbonic acid disengaged, even when that quantity is very small.

As to the decomposition of carbonates by acids, it is to be remarked that some of them are easily decomposed, others with much more difficulty. There are some which cannot be decomposed except after pulverisation and treatment with acids which must not be too concentrated but somewhat dilute and with the application of a gentle heat. The carbonates belonging to this class, which are found in nature, are the carbonate of

protoxyde of iron (spathose iron), and the combination of carbonate of lime and of magnesia (bitter spar dolomite).

\* When the operator wishes to determine the quantity of carbonic acid dissolved in a liquor, it may be done by means of a salt of lime, which produces a precipitate of carbonate of lime, or, better still, by means of that of a salt of baryta, which produces a precipitate of carbonate of baryta. This effect is produced both when the carbonic acid exists in the liquor in a free state, or in combination with alkalies in the state of carbonates, sesquicarbonates, or bicarbonates of these bases. The operator adds to the liquor a solution of chloride of calcium or of barium, and some ammonia, if the liquor contains free carbonic acid, or sesquicarbonates, or bicarbonates; if the operator is certain that only simple carbonates are present, this addition of ammonia is unnecessary. When it has been necessary to add ammonia, the precipitation must be performed in a flask capable of being hermetically closed. When the precipitate has completely settled, which requires several hours, the acid liquid is first poured on the filter, hot water is then added to the precipitate, and after having shaken it violently, it is allowed to settle again. This operation having been repeated several times, the precipitate is ultimately thrown on a filter. The funnel must be sheltered from the contact of the air during the filtering, in order to guard against the carbonic acid of the air augmenting the quantity of the earthy carbonate produced. The washing of the earthy carbonate is attended with a troublesome circumstance, namely, that it is impossible to know when it is complete, because neither of these two salts is completely insoluble in water. It is best, therefore, to wash the precipitate until the filtered liquor ceases to afford a precipitate when tested with a solution of nitrate of silver, to which a little free nitric acid has been added. The carbonate of lime produced is then treated as was said (page 25), in order to determine its weight, from which that of the carbonic acid may be calculated. With respect to the carbonate of baryta, it may be ignited,

burning the filter in the usual way, without fear of losing carbonic acid, owing to which the use of chloride of barium is preferable to that of chloride of calcium for this purpose.

\* If the solution in which the carbonic acid has to be determined contains sulphuric acid, phosphoric acid, or other acids which form with lime combinations which are sparingly soluble or altogether insoluble, these combinations are precipitated along with the carbonate of lime. If, besides carbonic acid, the liquor contains sulphuric acid only, instead of chloride of calcium, chloride of barium must be employed to effect the precipitation. The precipitate is then weighed, and treated by dilute muriatic acid, which leaves the sulphate of baryta in an insoluble state, the weight of which is determined, and from the loss that of the carbonate of baryta is estimated. If the precipitate of baryta contains other acids, for example, phosphoric acid, it must be ignited, and the quantity of the carbonic acid is determined in it by means of the methods which have been explained before, (pages 542, 543). The phosphoric acid is subsequently determined from the loss (page 438), that of the carbonic acid being already known.

## CHAPTER XLVII.

## BORON.

## DETERMINATION OF BORACIC ACID.

THE quantitative determination of boracic acid is attended with numerous difficulties. When this acid exists in a solution which contains no other acid, or which contains nitric acid only, it may be determined by the same method which is employed for arsenic and phosphoric acids, that is to say, an accurately weighed quantity of pure protoxyde of lead, recently ignited, is added to the liquor, which is evaporated to dryness, and the residuum is ignited in a small counterpoised platinum capsula. The quantity of the boracic acid is afterwards determined by deducting the weight of the protoxyde of lead which was added from that of the calcined mass.

Boracic acid cannot be quantitatively determined by evaporating the liquor to dryness, because a portion always volatilises along with the aqueous, and especially with the alcoholic vapours, if the acid was in solution in this menstruum.

There is no method of determining immediately the quantity of boracic acid in solutions by precipitating it in the state of an insoluble combination from which its quantity might be calculated. There is no base which can form with it a combination perfectly insoluble in water. In order, therefore, to estimate as accurately as possible this acid in borates, it is necessary to

determine what quantity of the bases or of substances are combined with the boracic acid, the quantity of this acid being estimated from the loss.

#### SEPARATION OF BORACIC ACID FROM METALLIC OXYDES.

The separation of boracic acid from the metallic oxydes which can be completely precipitated from an acid solution by sulphuretted hydrogen, or from a neutral or an alkaline solution by hydrosulphuret of ammonia, is effected in the same manner as that of the same oxydes from phosphoric acid. The methods which should be adopted have been described, (pages 429, 432).

#### SEPARATION OF BORACIC ACID FROM PROTOXYDE OF LEAD, LIME, STRONTIA, AND BARYTA.

Boracic acid is separated from baryta by sulphuric acid, and it might, perhaps, be separated from strontia, lime, and protoxyde of lead by the method employed for separating these bases from arsenic and phosphoric acids (pages 344, 439).

#### SEPARATION OF BORACIC ACID FROM THE FIXED BASES.

Boracic acid may be separated from its combinations with fixed bases, when such combinations are decomposable by concentrated sulphuric acid, which is the case with most of these, by a method which was indicated by Arfvedson, and which is as follows:—A certain portion of the combination, reduced into very fine powder, is weighed, and mixed in a platinum crucible or capsula, with three or four times its weight of fluor spar, also pulverised, but which must be extremely pure, and particularly free from silicic acid. A sufficient quantity of concentrated sulphuric acid is poured on the mixture, to produce, by stirring it with a platinum spatula, a thick magma. The whole is then heated to redness until no more vapours are evolved. The boracic acid is thereby converted into fluoboric gas (*fluoride borique*)

and is completely disengaged; the excess of the sulphuric acid employed is also volatilised towards the end, when the crucible is red hot. All the bases of the combination remain united with the sulphuric acid mixed with the whole of the sulphate of lime due to the decomposition of the fluor spar, and the respective quantities of each of the bases is afterwards determined by the methods which have been indicated before. After having determined them accurately, the quantity of the boracic acid is estimated from the loss. If the bases form with sulphuric acid compounds which are pretty easily soluble in water, the ignited mass is ordinarily washed until it is thought that the portion of sulphate of lime which remains undissolved is freed from the other more soluble sulphates. Oxalate of ammonia is then poured in the filtered liquor in order to precipitate the lime of the sulphate of lime which has dissolved, and the relative proportions of the bases are subsequently determined.

It may be easily perceived that all the borates which contain no water, and which are decomposable by sulphuric acid may be thus analysed. Those which contain lime may be treated in the same manner provided the quantity of the pure fluor spar added be rigorously weighed, in which case the operator deducts from all the lime obtained that which existed in the fluor spar employed.

In all such cases it would be much more advantageous to employ fluoride of barium instead of fluoride of calcium, the latter, however, is much less expensive. But the best reagent is pure hydrofluoric acid, prepared in a platinum retort, and which was employed by Berzelius for decomposing the borates. The salt submitted to analysis is decomposed in a counterpoised platinum crucible, by a mixture of hydrofluoric and of sulphuric acid; the whole is heated and evaporated to dryness; the dry residuum is ignited, and the bases which were contained in the borate remain combined with the sulphuric acid.

## SEPARATION OF BORACIC FROM SILICIC ACID.

When a combination contains both boracic and silicic acid and can be decomposed by acids, the above methods will only yield the collective quantities of these two acids. A fresh portion of the compound must therefore be devoted to the determination of the silicic acid, which is effected by decomposing the combination by means of muriatic acid, which leaves the silicic acid in an insoluble state, the weight of which may then be determined. It is better, however, to evaporate to dryness the combination, after having decomposed it by muriatic acid, as just said; moisten the dry mass with muriatic acid, and proceed to the determination of the silicic acid only after having treated by water the above moistened mass.<sup>1</sup>

When a combination contains water besides boracic and silicic acid, which is the case, for example, with the minerals called datholite and botryolite;<sup>2</sup> a third portion is devoted to the determination of the quantity of that water. To effect this it is sufficient to ignite the combination in a platinum crucible; the loss of weight indicates the quantity of the water.

<sup>1</sup> The evaporation should be carried on in a flask, and the vapours which disengage should be received in water, since boracic acid volatilising with the vapour, a loss would thus be sustained.—Ed.

<sup>2</sup> Datholite is a combination of silicic acid, boracic acid, lime and water. The analysis of this mineral by Dumenil, and Rammelsberg, gave the following results :—

	From Andreasberg in the Harz.		From Arendal in Norway.
	Dumenil.	Rammelsberg.	Rammelsberg.
Boracic acid . .	21·34	20·315	21·377
Silicic acid . . .	38·51	38·477	37·520
Lime . . . .	35·59	35·640	35·398
Water. . . . .	4·60	5·568	5·703
	100·04	100·000	100·000

Botryolite is a mineral found at Arendal in Norway, it is also a combination of boracic acid, silicic acid, lime and water, which, according to Rammelsberg, is

Yet, the quantitative determination of boracic acid presents very great difficulties when it exists in silicious compounds which cannot be decomposed by acids. It is more difficult still if the boracic acid is only in very small quantity, which is ordinarily the case. The minerals called tourmaline and axinite<sup>1</sup> are examples of this case.

generally mixed with carbonate of lime. The latter substance being removed, the above chemist gives the following results of his analysis of botryolite :—

Boracic Acid . . . . .	18.34
Silicic Acid . . . . .	36.90
Lime . . . . .	34.27
Water . . . . .	10.22

99.73—Ed.

See Berzelius, (page 343, vol. iv.)

<sup>1</sup> Tourmaline is a combination of silica, alumina, oxyde of iron, lime, with small portions of magnesia, potash, soda, and boracic acid ; Gmelin analysed samples of this mineral from St. Gothard, Karinbricks in Sweden, and Greenland ; the result of these analyses are given by him as follows, in the "Annales des Mines" :—

	Greenland.	Karinbricks.	St. Gothard.
Soda . . . . .	3.15	2.53	1.20
Potash . . . . .	0.22		
Silica . . . . .	38.79	37.65	37.81
Alumina . . . . .	37.19	33.46	31.61
Protoxyde of Iron . . . .	5.81	9.38	17.77
Protoxyde of Manganese .	0.00	0.00	1.11
Boracic Acid . . . . .	3.63	3.83	4.18
Magnesia . . . . .	5.86	10.89	5.99
Lime and loss . . . . .	1.86	0.25	0.98
	96.51	97.99	100.65

Axinite is a combination of silica, alumina, lime, oxyde of iron, manganese, and a smaller quantity of boracic acid, than the above. Wiegman gives the following analysis of the axinite of Trueburg :—

Silica . . . . .	45.80
Alumina . . . . .	19.00
Lime . . . . .	12.50
Protoxyde of Iron . . . .	12.25
Protoxyde of Manganese . .	9.00
Magnesia . . . . .	0.25
Boracic Acid . . . . .	2.00

100.00—Ed.



The analysis of such compounds gives only approximative results.

C. G. Gmelin employed the following method for determining the quantity of the boracic acid in the tourmalines. The substance is first reduced into very fine powder by levigation, and mixed with carbonate of baryta, and the whole is violently ignited. The ignited mass is then treated by as much muriatic acid as is necessary to effect its decomposition, and the acid liquor is evaporated to dryness in a water-bath. The quantity of the boracic acid which volatilises is so trifling, according to Gmelin, that it may be neglected. The silicic acid is separated from the residuum in the usual manner. The filtered liquor is mixed with an excess of a solution of carbonate of ammonia, which precipitates the baryta; the liquor is filtered, evaporated to dryness, and heated to incipient redness. No boracic acid can be lost during this experiment, because it is combined with ammonia, and no acid vapours containing water are disengaged during the ignition, as is the case when sulphate of ammonia is treated in the same manner; wherefore the baryta must be removed, not by sulphuric acid, but by carbonate of ammonia. The dry residuum is then weighed, alcohol and a little muriatic acid is poured upon it, and the alcohol is set fire to. This operation is repeated until the flame of the alcohol ceases altogether to have a green tinge on the edges. The boracic acid is thus entirely expelled; it was contained in the solution in the state of borate of ammonia, but this salt was converted into free boracic acid by ignition. The residuum is again ignited and weighed; the loss indicates the quantity of the boracic acid.

*Another method* proposed by Gmelin for the determination of boracic acid in these combinations, consists in igniting the pulverised compound with carbonate of soda, lixiviating the ignited mass with water, and precipitating by digestion with a solution of carbonate of ammonia the small quantities of

alumina and of silicic acid which the water has dissolved. The liquor is then evaporated to dryness, sulphuric acid is poured on the dry mass, and the boracic acid is dissolved by digesting with alcohol; the solution is then saturated by ammonia; the residuum, which consists of boracic acid, is then ignited and weighed.

## CHAPTER XLVIII.

## FLUORINE.

## DETERMINATION OF FLUORINE.

THE safest method of determining fluorine in its combinations, consists unquestionably in weighing a certain portion of such combinations, pouring concentrated sulphuric acid upon them, and heating until the whole of the fluorine has been expelled in the state of hydrofluoric gas, and likewise the excess of the sulphuric acid employed. The metal which was combined with the fluorine remains then in the state of sulphate.

It is necessary to perform this experiment in a crucible of platinum, and not in a vessel containing silica. The quantity of the metal is calculated from that of the sulphate, and the loss indicates that of the fluorine. When fluorine is combined with more than one metal, the combination is likewise decomposed by sulphuric acid, but the sulphates obtained must be submitted to a separate analysis, in order to determine from their combination that of the compound of fluorine.

When a fluoride contains water of crystallisation, the quantity of the latter may in many cases be determined from the loss sustained by igniting a weighed portion of the compound. In a great number of cases, however, the united action of the atmospheric air and of the water produces a partial

decomposition ; part of the fluorine is disengaged with water in the state of hydrofluoric acid.

In order to prevent this, and to determine with great accuracy the quantity of the water of crystallisation contained in a fluoride, a portion of the latter is mixed with about six parts of a very finely pulverised and recently ignited protoxyde of lead. The mixture is introduced into a small glass retort, and covered with a little protoxyde of lead, and the whole is then ignited. The water is then disengaged without any trace of acid. The retort, which should have been previously weighed when empty, is weighed again after the introduction of the fluoride for examination and ignited, and upon weighing it again, after complete cooling, the loss of weight indicates the quantity of the water. The ignition must be performed in a small retort because fluoride of lead undergoes a slight decomposition when ignited in the air.

Berzelius has always employed this method for determining the quantity of the water of crystallisation of the fluorides.<sup>1</sup>

#### SEPARATION OF FLUORIDES FROM HYDROFLUORIC ACID.

When the combination of fluorine and a metal to be analysed contains hydrofluoric acid besides, the quantity of the latter may, in a great number of circumstances, be determined from the loss which a given weight of the combination sustains at ignition, in a platinum crucible. There always remains metallic fluoride. Yet, as in a great number of cases,

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<sup>1</sup> Wöhler proposed another method for the determination of fluorine, which consists in adding pure silicic acid to the compound (if it is not already a silicate). The substance or the mixture in question is put in an exactly weighed flask, and very concentrated sulphuric acid, previously boiled, is added ; the flask is then immediately closed with a cork connected with a tube containing chloride of calcium, and the extremity of which is drawn to a point. The apparatus, having been weighed, is heated until the whole of the hydrofluosilicic acid is disengaged, the last portions of which are expelled by means of a pump. The operation being finished, the apparatus is weighed again, and the loss indicates the quantity of fluoride of silicon produced from which that of the fluorine is calculated. 1.000 of fluoride correspond to 1.000 of fluoride of silicon.—Ed.

metallic fluoride which remains, undergoes a slight decomposition by ignition in the air, Berzelius, in order to determine the quantity of hydrofluoric acid, always mixes with it about six times its weight of protoxyde of lead finely pulverised, and recently ignited, and he then ignites the whole. The hydrogen of the hydrofluoric acid combines with the oxygen of the protoxyde of lead to form water, which water is not acid. In order to determine the quantity of this water, the operator proceeds exactly in the same manner, as for the determination of the water of crystallisation contained in the fluorides. From the quantity of this water, that of the hydrofluoric acid contained in the compound under analysis is easily calculated. Another portion of the combination is then decomposed by sulphuric acid, and from the quantity of the sulphate obtained, the collective proportion of the fluorine, and of the hydrofluoric acid, becomes known, from which that of the fluorine may most easily be estimated.

When the combination of the metallic fluoride with hydrofluoric acid contains water of crystallisation besides, the water which is obtained by treating the combination by protoxyde of lead consists of the water of crystallisation and of the water produced by the combination of the hydrogen of the fluoride, with the oxygen of the protoxyde of lead. Another portion of the combination is then decomposed by means of sulphuric acid, and from the quantity of the sulphate obtained, that of the fluorine of the hydrofluoric acid, and of the water of crystallisation is collectively determined. Lastly, the combination which has been ignited with the protoxyde of lead, is decomposed by sulphuric acid, and the quantity of the fluorine contained in the metallic fluoride, and in the hydrofluoric acid, is determined.

The determination of the fluorine contained in a combination which is dissolved in water, is more difficult. When this combination is kept in solution, not by another acid, but merely by free hydrofluoric acid, and is capable of being decomposed by ebullition with carbonate of alkali, or with a solution of pure

potash, the excess of alkali might be saturated by an acid, and on pouring a solution of a salt of lime in the liquor, the whole of the fluorine contained in the fluoride of potassium produced would be precipitated in the state of fluoride of calcium, from the weight of which the quantity of the fluorine might then be calculated.<sup>1</sup> The determination of the fluorine contained in such fluorides held in solution, is very seldom required; I shall, however, detail farther on the precautions which should be employed in such cases.

#### SEPARATION OF FLUORINE FROM BORON.

It is very difficult to analyse quantitatively the combinations of fluorine with boron, and the combinations of fluoride of boron, with the metallic fluorides. When they are decomposed in the same manner as the metallic fluorides by sulphuric acid, with the help of heat, the quantity of the fluoride of boron, and of the fluorine which were combined with the metal of the oxyde produced during the reaction, may be determined from the quantity of the sulphate obtained. When these substances contain water of crystallisation, the quantity thereof is determined by means of protoxyde of lead, in the same manner as is done for a metallic fluoride. These combinations cannot be decomposed by treating them with a solution of carbonate, or of hydrate of potash. When heated in a retort, there remains a metallic fluoride, whilst fluoride of boron is disengaged. The quantity of this metallic fluoride might be determined, and from its weight, the composition of the combination might be calculated; but it is very often extremely difficult to decompose these combinations in a complete manner, by igniting them in the manner which has been described.

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<sup>1</sup> The precipitate is gelatinous, and should be washed with hot water, and then, in order to remove the carbonate of lime which might contaminate the precipitate by the action of the carbonic acid of the atmosphere, the washing is finished with dilute acetic acid, after which the precipitate is dried, ignited and weighed.—Ed.

## SEPARATION OF FLUORINE FROM SILICIUM.

The combination of fluorine with silicium, but principally the compounds which fluoride of silicium forms with the metallic fluorides, are more easy to analyse. The composition of an aqueous solution of fluoride of silicium may, according to Berzelius, be determined as follows:—

To the acid liquor add a solution of carbonate of soda, until it ceases to produce an effervescence; this produces a precipitate of silicifluoride of sodium, which is sparingly soluble, and which is collected upon a weighed filter, and washed. It is then dried in a counterpoised platinum crucible, in order not to lose that portion of the dissolved salt contained in the pores of the paper. When dry, its quantity is determined, from which, that of the silicium, and of the fluorine, is calculated. The solution which was saturated with soda, is then supersaturated with carbonate of soda, after which, a solution of carbonate of zinc in pure ammonia is added, and the whole is evaporated almost to dryness. The oxyde of zinc combines with the silicic acid, and produces a silicate which, when the mass is treated by hot water, remains insoluble, and may be washed without fear of loss. After the washing, the silicate of zinc formed is decomposed by nitric acid, and the whole is evaporated to dryness, in order to render the silicic acid absolutely insoluble; the dry mass is then treated by acidulated water, which dissolves the nitrate of zinc. The silicic acid remains in an insoluble state, and is collected upon a filter; it is then washed, ignited, and weighed. From its quantity, that of the silicium is calculated.

The alkaline liquor which was filtered from the silicate of zinc, and which contains fluoride of sodium and carbonate of soda, is saturated by acetic acid, yet without completely saturating it, in order to avoid all possible loss of hydrofluoric acid during the evaporation. After having evaporated it carefully to dryness, a mixture of weak alcohol and of acetic acid is

poured on the dry residuum. The small quantity of carbonate of soda which existed still in the dry mass, because the alkaline liquor had not been completely saturated, is thereby converted into acetate of soda. The whole of the latter salt dissolves in the alcohol, whilst the fluoride of sodium remains; the latter is washed with alcohol, dried, ignited, and weighed. From its weight that of the fluorine is calculated.

All these operations being performed, it is then easy to calculate from the results obtained, the quantity of the constituents of the aqueous solution of the fluoride of silicium.

The gaseous combination of fluorine and of silicium may be quantitatively analysed, by passing the gas in water, which precipitates the silicic acid. The stream of gas may be continued until the liquor becomes so thick with the liberated silicic acid, that it cannot absorb any more of it. It is necessary, in this experiment, that the disengagement tube should not touch the water, for it would soon be obstructed. The absorption of the gas is promoted by agitating the liquor frequently; the extremity of the tube may be conveniently placed under mercury, over which water has been poured, which absorbs the gas. When the liquor has become as thick as pap, it is diluted with water, and the liberated silicic acid is collected on a filter and washed until the filtrate ceases to redden litmus paper. The silicic acid which remains after perfect washing, contains no trace of hydrofluoric acid; it is then dried, ignited, and weighed. The filtered liquor is afterwards treated as we have just said.

#### SEPARATION OF FLUORIDES OF METALS FROM FLUORIDE OF SILICIUM.

The combination which fluoride of silicium forms with metallic fluorides, may be analysed in various ways in the dry state. By treating them with sulphuric acid, with the help of heat, and volatilising completely the excess of the sulphuric acid employed, all the fluorine and silicium are disengaged in



the state of fluoride of silicium, whilst the metal of the fluoride, which has thus been converted into oxyde, remains combined with the sulphuric acid. Most of these combinations are rapidly decomposed when treated by sulphuric acid, and produce a violent disengagement of fluosilicic gas. Yet some of them, such as, for example, the fluoride of silicium and calcium, and the fluoride of silicium and of barium require the application of heat. The quantity of the sulphate obtained is determined from which that of the metal is calculated; the quantity of the water of crystallisation, if any existed in the compound, must be deducted.

The dry combinations of fluoride of silicium with metallic fluorides, may also be analysed by igniting them. Fluosilicic gas is then evolved, whilst the metallic fluoride remains, from the weight of which the composition of the compound may be calculated, when it contains no water of crystallisation. A strong heat, which must be continued for a long time, is, however, requisite, in order to expel the whole of the fluoride of silicium. When the combination is ignited in the air, the metallic fluoride which remains contains free silicic acid; because the slightest trace of moisture in the air separates silicic acid from the fluoride of silicium, which silicic acid is subsequently dissolved by the fused metallic fluoride. This effect is produced to a greater extent, when the experiment is performed in an open platinum crucible, heated by means of an argand spirit-lamp, because the combustion of alcohol produces water. It is on this account that when, in such experiments, the remaining metallic fluoride had to be weighed in order to determine the composition of the compound, Berzelius introduced three closed platinum crucibles within each other, the substance being placed in the innermost crucible, and heated the whole upon a charcoal fire. The inner side of the exterior crucible was then found thickly incrustated with silicic acid.

When the combinations of fluoride of silicium and of

dried, and then mixed with four times its weight of carbonate of soda in a platinum crucible, and the whole is to be exposed to a full red heat for a long time. After cooling, the mass is withdrawn from the crucible, and softened by water, and the portions which refused to dissolve are separated by filtering, and washed with water until it ceases to have an alkaline reaction upon litmus paper. It is often impossible to wash this residuum so perfectly that upon evaporating a few drops of the filtrate upon a platinum foil, no residuum will be left. Carbonate of ammonia is added to the filtered liquor which, besides fluoride of silicium, and the excess of carbonate of soda employed, contains also traces of silicic acid, and even of alumina; hence a slight precipitate, which ordinarily augments a little on evaporating the liquor. The precipitate is collected on a filter as small as possible, and washed. It is then treated, as well as the residuum insoluble in water previously obtained, by muriatic acid, by which it is easily and completely decomposed. When a concentrated acid has been employed, the silicic acid ordinarily separates in the form of a jelly. The whole is then evaporated to perfect dryness; after cooling, the dry mass is moistened uniformly with muriatic acid, and water is added to it after some time. The silicic acid remains undissolved; it is collected on a filter, and its weight is determined. The filtered liquor contains all the bases which existed in the substances submitted to analysis in the state of solution in muriatic acid, which bases may then be determined by the methods which have been described before.

The quantity of fluoride of silicium contained in the alkaline liquor, which alkaline liquor contains still some carbonate of soda besides, might be determined by the method which I have described before, and which consists in saturating the liquor by acetic acid, and separating the acetate of soda from the fluoride of sodium by means of alcohol. When, however, the quantity of the metallic fluoride contained in the combination under examination is considerable, it is preferable to resort to another method; the alkaline liquor is evaporated until it is reduced to a

somewhat small volume, and it is then moderately supersaturated with muriatic acid. This operation must be performed in a silver, or better still, in a platinum capsula, and the mixture must be stirred with a spatula of silver or of platinum. The vessel is then covered with a piece of filtering paper, and the liquor is left at rest for twenty-four hours without heating it: the carbonic acid is thereby completely expelled. In order to make sure of this, the capsula containing the acid liquor may be put upon a stove slightly warm, taking care that the temperature does not exceed  $30^{\circ}$  cent. This time having elapsed, the liquor is then slightly supersaturated in the capsula with pure ammonia, and poured in a bottle which admits of being hermetically closed with a cork. A solution of chloride of calcium is then added, and the bottle is corked up, which produces a deposit of fluoride of calcium. In order to guard against this salt being contaminated by carbonate of lime, the liquor must be previously freed from all carbonic acid, and further, after having added the chloride of calcium, it must be sheltered from the contact of the air. When the fluoride of calcium has completely settled at the bottom of the bottle, the clear supernatant liquor is decanted and replaced by water previously freed from atmospheric air by boiling, and the bottle is corked up again. When the fluoride of calcium has again deposited, it is collected upon a filter, washed, ignited, and weighed. From the quantity obtained, that of the fluorine contained in the combination is calculated.

It is always necessary to ascertain that the ignited fluoride of calcium is pure. It should be moistened with a little water in a platinum crucible, and muriatic or acetic acid should be added, in order to see whether any effervescence will take place, which would indicate the presence of carbonate of lime. If a strong effervescence is thus produced, alcohol should be poured upon the fluoride of calcium which was treated by the acetic acid; it should be washed again by alcohol, dried, ignited, and weighed. In this manner only can the exact quantity of the fluorine contained in the combination be arrived at.

The precipitated fluoride of calcium may sometimes contain a small quantity of silicic acid. The absence of this acid is proved when the salt, after having been ignited, does not evolve the slightest heat when moistened with pure hydrofluoric acid; if the slightest trace of silicic acid is present, heat is produced by this treatment. When native fluor spar is thus tested, in order to ascertain whether it contains silicic acid or not, it should be previously reduced into powder.

In precipitating fluoride of calcium from an ammoniacal liquor, by means of a solution of chloride of calcium, the precipitate is often gelatinous, and on that account cannot be washed, because it obstructs the pores of the paper. This jelly is so translucent that at first the precipitate appears very minute indeed, and when looked at transversely against day-light, it has a slightly reddish opaline tinge. This case occurs when the liquor to which chloride of calcium is added, contains only a very slight excess of ammonia. By leaving a larger proportion of ammonia in the liquor the fluoride of calcium is completely separated.

When the combination submitted to analysis contains a very large proportion of lime, or rather when the fluorine is combined with calcium, the whole of the fluorine cannot be obtained by fusing the compound with carbonate of soda. It would appear that carbonate of soda cannot effect the complete decomposition of fluoride of calcium.

The method which has just been described, may, however, be employed for the purpose of decomposing the combinations which do not contain too great a quantity of silicic acid. Carbonate of soda likewise separates silicic acid completely from the combinations which, besides metallic fluorides, contain tribasic or even sesquibasic silicates, because these latter salts are not soluble in a solution of carbonate of soda. But when the silicate is a neutral one, that is to say, when the silicic acid contains three times as much oxygen as the base with which it is united, the alkaline

carbonate dissolves a portion of the acid, and when the ignited mass comes to be treated by water, this menstruum, besides fluoride of sodium and carbonate of soda, dissolves silicate of soda also, whilst the bases are left in an insoluble state combined with the greatest part of the silicic acid. In order to separate the silicic acid from the silicate of soda dissolved in the liquor, a solution of carbonate of zinc in ammonia may be added, by which means the silicic acid is precipitated in the state of silicate of zinc. In such a case the determination of their bases is more difficult, because the operator has further to separate the oxyde of zinc which has been added. The silicates which have remained in an insoluble state when the ignited mass was treated by water, may however be decomposed by a separate operation, and the silicate of zinc may also be decomposed separately by means of nitric acid, in order to determine the silicic acid which it contains, which simplifies the analysis much.

Among the minerals which contain at the same time silicates and metallic fluorides, and which muriatic acid cannot decompose, the topaz is that which contains the greatest quantity of metallic fluoride,<sup>1</sup> smaller quantities are found in the mineral called chondrodite;<sup>2</sup> the several species of mica, of amphibole, and some varieties of scapolite.

When a combination of silicates and of metallic fluorides is

<sup>1</sup> Topaz is a combination of alumina, silica, and fluoric acid. A sample of Brazilian topaz analysed by Berzelius, gave—

Alumina . . . . .	58.38
Silica . . . . .	34.01
Fluoric Acid . . . . .	7.79
	<hr/>
	100.18

Mosander represents the composition of topaz as follows :—

Alumina . . . . .	57.73
Silica . . . . .	34.48
Fluorine . . . . .	14.71
	<hr/>
	106.92

<sup>2</sup> The presence of fluorine in chondrodite was first discovered by Seybert; but the analyses which Rammelsberg made of that mineral agree pretty closely with those

very easily decomposable by muriatic acid, this acid should be resorted to in the cold. It is important to avoid all external heat, which might cause a volatilisation of some fluoride of silicium. After having decomposed it by muriatic acid, if the liquor be evaporated to dryness, no trace of fluorine can be obtained, because the whole of that substance has volatilised in the state of fluosilicic gas. It is owing to this, that it has very often happened in analysing certain minerals, for example, that called apophyllite, a small quantity of fluorine has been completely overlooked.

When the quantity of the metallic fluorides in the combination submitted to analysis is not very considerable, which is always the case with the compounds of this kind which are found in

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made by Seybert, represent, it is believed, the composition of this mineral more accurately. We reproduce them here.

	Yellow Chondro- dite of South America.	Grey Chondro- dite of Pargas.	Yellow Chondro- dite of Pargas.
Silicic Acid . . . .	33·06	33·19	33·10
Magnesia . . . . .	55·46	54·50	56·61
Protoxyde of Iron .	3·65	6·75	2·35
Fluorine . . . . .	7·60	9·69	8·69
	<u>99·77</u>	<u>104·13</u>	<u>100·75</u>

Amphibole or Hornblende consists principally of silica (partially replaced by alumina), magnesia and lime. According to Bonsdorf, the components of that mineral are as follows :—

	Black.	Dark Green.
Silica . . . . .	45·69	47·21
Lime . . . . .	13·85	12·73
Magnesia . . . . .	18·79	21·86
Protoxyde of Iron . . .	7·32	2·28
Protoxyde of Manganese	0·22	0·57
Alumina . . . . .	12·18	13·94
Fluoric Acid . . . . .	1·50	0·90
	<u>99·53</u>	<u>99·49</u>

nature, the compounds are decomposed by muriatic acid, in the cold, in a platinum vessel, and the silicic acid is first separated. If the combination contains no alumina, nor peroxyde of iron, and in general if it contains lime only, and no substance capable of being precipitated by ammonia, if ammonia be poured in the liquor a precipitate is produced, which consists of a combination of fluoride and of silicate of lime. This precipitate is washed, dried, ignited and weighed. It contains one atom of silicate of lime, and two atoms of fluoride of calcium. Berzelius obtained it in the manner which has been described in analysing the mineral called apophyllite. Other chemists had until then mistaken it for alumina.

When on the contrary the combination contains other substances, which ammonia can precipitate, the operator must, after having separated the silicic acid by filtering, supersaturate the filtered liquor by carbonate of soda, with which it must be digested or boiled. Fluoride of sodium and carbonate of soda, are thus dissolved whilst the other constituents of the combination ordinarily remain in an insoluble state. The quantity of the fluorine is afterwards determined as was described above.

#### SEPARATION OF FLUORIDES FROM PHOSPHATES.

The fluorides which occur in nature are very often found combined with phosphates. Phosphoric acid is so frequently met with in the combinations of fluorine, that when the latter has been detected in a mineral, the operator should never omit to look for phosphoric acid, or *vice versd*. Berzelius found small quantities of phosphoric acid in native fluorides which had been looked upon as very pure; for example, he detected it in the purest fluor-spar. Again, some phosphates contain very small proportions of metallic fluorides, such as the mineral called Wavellite, and in bones.<sup>1</sup>

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<sup>1</sup> Wavellite is a combination of phosphoric acid, water, and alumina, sometimes

The methods employed for separating phosphoric acid from metallic fluorides, vary according to the nature of the other constituents of the combination. When the latter is decomposable by acids, and if it contains only very little fluorine and phosphoric acid, but a large quantity of silicates, it is ignited with carbonate of soda: the ignited mass is afterwards treated by water, as was said before. The alkaline liquor filtered from the insoluble residuum contains fluoride of sodium, phosphate, and carbonate of soda. The process for analysing it is the same as was described (page 562). The liquor is put in a bottle, which admits of its being hermetically closed, and a solution of chloride of calcium is added to it, which produces a precipitate consisting of a mixture of phosphate of lime, and of fluoride of calcium; this precipitate is washed, dried, ignited in a platinum crucible, and weighed.

The quantities of the two combinations contained in this precipitate may be determined as follows:—Concentrated sulphuric acid is poured upon the mixture in the platinum crucible in which it has been ignited and weighed, but too large an excess of sulphuric acid must be avoided. If no effervescence is produced in the cold, the mixture is free from silicic acid and carbonate of lime. The crucible is then heated until all the fluorine has disengaged in the state of hydrofluoric acid gas; it is known that the whole has been expelled when a small plate of glass, placed from time to time over the crucible, ceases to be attacked. The remaining acid mass is then treated by a very large quantity of water, which dissolves the excess of the sulphuric acid employed, the sulphate of lime produced at the expense of the fluoride of calcium, and the phosphoric acid. The solution

mixed with a little lime, oxyde of manganese, and of iron, and of fluoric acid. Fuchs gives the analysis of this mineral as follows:—

Phosphoric acid	34.72
Alumina	36.56
Water	28.00
	<hr/> 99.38



is put in a bottle which admits of its being closed, and slightly supersaturated with ammonia, which produces a precipitate of phosphate of lime. This precipitate is allowed to settle, taking care to keep the bottle well corked up, in order to exclude the atmospheric air. The precipitate is afterwards collected on a filter, and its weight is determined; the quantity of the phosphoric acid which it contains is afterwards estimated in the manner which was described before (page 439).

Oxalate of ammonia is now poured in the liquor which was filtered from the phosphate of lime, which precipitates, in the state of oxalate of lime, the lime which was combined before in the state of fluoride of calcium along with the phosphate of lime. This oxalate is converted into carbonate of lime by the method described (page 23), and from its quantity that of the fluoride of calcium is calculated.

The two salts may be determined in the precipitate of fluoride of calcium and of phosphate of lime in another way. The precipitate is treated, as was said before, by concentrated sulphuric acid, in order to disengage the hydrofluoric acid; alcohol is then poured upon the acid mass which remains in the platinum crucible, which leaves the sulphate of lime produced in an insoluble state, but dissolves the phosphoric acid, and the excess of sulphuric acid employed. The sulphate of lime is washed with alcohol, and its weight is determined. Ammonia and water are then added to the alcoholic solution, it is submitted to a very gentle heat, in order to volatilise the alcohol, more water is poured in, and a solution of chloride of calcium is added, which produces a precipitate of phosphate of lime, whilst the sulphate of lime remains in solution, provided, of course, a sufficient quantity of water has been added. When the liquor contains still an excess of ammonia, the precipitation by means of chloride of calcium should take place in a bottle corked airtight, in order that the phosphate of lime may be deposited out of the contact of the air. The quantity of this phosphate

is determined in the manner which has been described (page 439), from which the quantity of the phosphoric acid is determined. The operator having calculated from the weight of the sulphate of lime, the quantity of phosphoric acid and of the lime contained in the precipitate, which consists of fluoride of calcium and of phosphate of lime, it is easy to calculate the relative quantities of the two salts of which the precipitate consists.

\* When a silicate which contains small quantities of fluorides and of phosphates is decomposable by muriatic acid, this reagent may be employed to decompose it, in the cold, in a platinum crucible; the liberated silicic acid is collected on a filter. If the filtered liquor contains neither alumina nor peroxyde of iron, nor any other substance capable of being precipitated by ammonia, but contains lime only, the addition of ammonia, besides fluoride of calcium and silicate of lime, precipitates phosphate of lime also. The precipitate is weighed; it is put in a platinum crucible, and treated therein by sulphuric acid with the help of heat, which disengages fluosilicic gas. Water is now poured upon the mass, which (the water) dissolves not only the excess of sulphuric acid employed, but likewise the sulphate of lime produced, and the phosphoric acid. Ammonia is now poured in the solution, by which phosphate of lime is precipitated. It is then collected on a filter, and oxalate of ammonia is added to the filtered liquor, in order to precipitate the lime which it holds in solution. This lime existed in the state of fluoride of calcium and of silicate of lime in the precipitate produced by the ammonia, and in the proportions which have been indicated before (page 567).

It is only those combinations which contain very little phosphoric acid and fluorine, and of which these substances do not form an essential part, which can be analysed by the method above. If the quantity of the phosphoric acid is more considerable, most of the bases cannot be separated from their

solutions so completely as not to retain any trace of the acid. In such a case the combination must be ignited with carbonate of soda.

This method of analysis must be adopted also when the combination contains no silicic acid. If alumina, however, forms part of the constituents of that substance, which is the case with the mineral called Wavellite, it must be fused with carbonate of soda and silicic acid, as was said (page 562). The ignited mass is afterwards treated by water, which dissolves the carbonate of soda, and also the fluoride of sodium, and the phosphate of soda produced, and in which the quantity of the fluorine, and of the phosphoric acid, may be determined by the methods which have been indicated above.

#### SEPARATION OF FLUORIDES FROM SULPHATES.

Some fluorides, for example, fluor spar, occur in nature accompanied by sulphates. If the sulphate is heavy spar,<sup>1</sup> it is sufficient to treat the substance by muriatic acid in a platinum vessel; the fluor spar dissolves, but the heavy spar remains insoluble upon diluting the liquor with water, and its quantity may then be determined. The muriatic solution of the fluor spar may subsequently be mixed with sulphuric acid, and the whole evaporated to dryness, which produces sulphate of lime, from the weight of which the quantity of fluor spar is calculated.

When the sulphates dissolve in muriatic acid, and in water, along with the fluorides, the diluted acid solution is introduced into a platinum vessel, and mixed with a solution of chloride of barium, by which means the quantity of the sulphuric acid is determined. The bases are found by treating another portion of the substance by sulphuric acid, which converts them into sulphates.

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<sup>1</sup> Sulphate of baryta.

## CHAPTER XLIX.

## CHLORINE.

## DETERMINATION OF CHLORINE GAS IN A FREE STATE.

It is extremely difficult to determine the volume of free chlorine gas, because it is taken up both by water and by mercury; and neither of these two liquids can therefore be employed to collect it. The best method consists in carefully receiving it, as soon as it is disengaged, into ammonia diluted with water. Part of the alkali is thereby decomposed, and muriate of ammonia is formed, which remains dissolved whilst nitrogen is evolved. The operator must take care that the chlorine disengages as slowly as possible, in order that the decomposition may be complete, and that no chlorine may escape with the nitrogen. The best method is to pour the ammonia in a very capacious vessel, and to close it with a cork, traversed by the tube through which the chlorine is admitted. The cork must not close the bottle air-tight, in order that the nitrogen may escape. It is necessary that the ammonia be in excess, in order to prevent the formation of chloride of nitrogen. When the disengagement of chlorine has ceased, all the chlorine contained in the disengagement tube and in the bottle from which this gas is produced is expelled by means of carbonic acid, in order to convert that portion of chlorine also into muriate of ammonia. The operator may proceed in the manner indicated (page 387), for the absorption of sulphuretted hydrogen by metallic solutions. The ammoniacal solution is afterwards

acidified by means of nitric acid, and the chlorine is determined as in those of its combinations which are soluble in water by means of nitrate of silver, as will be shown presently.

\* When free chlorine exists in solution in water or in another liquid, the solution is rendered ammoniacal, and it is then treated in the same manner.

DETERMINATION OF CHLORINE IN COMBINATIONS WHICH ARE SOLUBLE IN WATER.

In order to determine chlorine quantitatively in its combinations with metals and with hydrogen, the operator begins, if the combination is soluble in water, by dissolving it, and he then adds a solution of nitrate of silver, which produces a precipitate of chloride of silver, from the weight of which the chlorine is estimated. The precautions which must be observed in the quantitative determination of that substance, and especially in the fusion of the chloride of silver, have already been described before (page 197).

It is advisable, and in a great number of cases it is absolutely necessary, to acidify slightly the aqueous solution of the combination of the chlorine before precipitating it by nitrate of silver. Dilute nitric acid is ordinarily employed for the purpose. The loss of this acid is not attended with any inconvenience when it is not very concentrated, and when the solution of the chlorine is sufficiently dilute.

After having separated the chlorine in the state of chloride of silver, by pouring a solution of silver in the combination which contains it, the quantity of the metals which were combined with the chlorine are determined in the filtered liquor, in which they then exist in the state of metallic oxydes. This is done by the methods which have been described in full before. Yet, before separating the metallic oxydes, it is necessary, in most

cases, to eliminate the excess of the solution of oxyde of silver employed; muriatic acid must therefore be poured into the filtered liquor, and the chloride of silver thus precipitated by this reagent must then be separated by filtering, and the operator proceeds to the determination of the metallic oxydes contained in the filtrate.

#### DETERMINATION OF CHLORINE IN ITS VOLATILE COMBINATIONS.

When very volatile combinations of chlorine have to be analysed, for example, chlorides of phosphorus, of sulphur, of selenium, of tellurium, of arsenic, of chromium, of titanium, of antimony, of tin, &c., they must likewise be dissolved in water. Most of them, even when decomposed by water, dissolve therein and give a clear solution. With a few, however, this is not the case. For example, the chlorides of sulphur, and one of the chlorides of selenium, deposit sulphur and selenium when treated by water. Treated in the same manner, chloride of phosphorus (*chloride phosphoreux*) ordinarily deposits a little phosphorus, and chloride of tellurium leaves a residuum of tellurous acid, and of metallic tellurium.

If the volatile combinations of chlorine are decomposed when treated by water, but dissolve therein completely, the operator proceeds absolutely as for the metallic chlorides, which are not decomposable by water. Ordinarily a little nitric acid is added to the liquor, and in order to determine the chlorine, a solution of nitrate of silver is poured, and after having removed the excess of reagent which may have been employed, by means of muriatic acid, the substance which was united to the chlorine in the combination submitted to analysis is determined.

Great difficulties, however, are encountered, both in weighing very volatile metallic chlorides and in dissolving them in water, which difficulties should be guarded against, or else a loss will take place. As the volatile combinations of chlorine quickly evaporate in the air, they must be weighed out of its contact.

The mixing of such volatile chlorides with water especially require the utmost precaution, for most of them produce a very considerable disengagement of heat, which may easily volatilise a great portion of the muriatic acid produced by the reaction. The best is, therefore, to proceed as follows for weighing the chlorides which are volatile and liquid, and which have to be mixed with water. The operator blows at the end of a tube of thin glass a small bulb, drawn out to a long and very fine point. The bulb is first weighed and then heated as strongly as the glass will permit without fusing; the point is then suddenly plunged in the volatile chloride, which ascends into it as the bulb cools. The point is then withdrawn, well dried, and the small apparatus is again weighed, which indicates the exact quantity of substance employed in the experiment. The point of the bulb must be so fine that no evaporation can take place during the weighing. This being done, the bulb is put into a bottle containing water, capable of being hermetically closed with a glass stopper, and shaken therein until it breaks. The chloride which it contained mixes then with the water, without the possibility of any portion of the combination itself of the chloride of the muriatic acid produced being lost, taking care, of course, that the stopper is not expelled by the action of the chloride upon the water. After complete cooling, the bottle is carefully emptied, so as to leave the pieces of the broken glass bulb behind, and it is rinsed with water.

If the very volatile chloride is not liquid but solid, as, for example, chloride of phosphorus (*chloride phosphoreux*), it is more difficult to weigh it. It is then introduced, as well as possible, in a glass stoppered bottle, previously weighed with the stopper, and it is then introduced, without the stopper, into a larger bottle containing water which is to be immediately closed.

The liquid chlorides, which are easily decomposed by a gentle heat, and which consequently cannot be introduced with those mentioned before in a small glass bulb, may be weighed in the same manner.

Most of these volatile chlorides are decomposed by water, the result being, that the hydrogen of the liquid combining with the chlorine forms muriatic acid, whilst the oxygen of the liquor unites with the body which was combined with the chlorine, and converts it in almost every case into an acid, which dissolves in the water or in the muriatic acid produced. When the operator knows how much oxacid has been produced by the reaction, it is very easy to estimate the composition of the chloride. If this quantity of oxygen is unknown, it is sufficient to determine the quantity of the muriatic acid which has formed, by precipitating it in the state of chloride of silver by means of a solution of nitrate of silver. The loss indicates, not only the quantity of the body which was combined with the chlorine, and consequently the composition of the chloride, but the quantity of the oxygen contained in the oxyde produced by the decomposition of the water, may also be easily calculated.

\* The operator must, however, be careful not to apply these conclusions to those volatile chlorides for the preparation of which a body containing oxygen has been employed. In effect, such combinations, besides a pure chloride, may contain an oxacid or an acid of the metal, united to the chlorine in the chloride. It also very often happens that the presence of the oxacid or of the oxyde cannot be easily shown otherwise than by dissolving a known weight of the combination in water, and determining the quantity of muriatic acid produced, and that of the oxacid or of the oxyde contained in the solution. If, after having calculated the quantity of the chlorine, and that of the metal, there is still a considerable loss, it must consist of oxygen, which has formed an acid or an oxyde with part of the metal.

The method of analysis of the chlorides which are soluble in water may be used in most cases as has been already remarked. There are some chlorides, however, for the analysis of which another process must be adopted. We shall treat of each of these chlorides successively.



Among the chlorides which are soluble in water there are several for the analysis of which it is absolutely necessary to eliminate, or to determine quantitatively, the oxyde or the oxacid which has been produced by the reaction, before the precipitation of the chlorine in the state of chloride of silver can take place. When these combinations have been converted by water into oxydes or oxacids, it often happens that the addition of an excess of solution of silver produces a precipitate, not only of chloride of silver, but likewise of a combination of oxyde of silver with the oxyde or oxacid produced. This combination is sometimes very sparingly soluble in the free nitric acid which is added to the liquor, whilst in other cases it is easily soluble therein.

#### SEPARATION OF CHLORINE FROM PHOSPHORUS AND FROM ARSENIC.

When proto and perchloride of phosphorus, or chloride of arsenic are decomposed by water, it is only necessary to add a sufficient quantity of nitric acid to the solution before pouring the solution of nitrate of silver, by which means the chloride of silver is precipitated, free from phosphate, and from arseniate of silver. This addition of nitric acid to the solution of the protochloride of silver prevents also the reduction of metallic silver by the phosphorous acid produced. As the determination of the acids of phosphorus and of arsenic presents difficulties, and especially as the presence of the muriatic acid which the operator was obliged to employ to precipitate the excess of oxyde of silver, renders it difficult to determine the quantities of both phosphoric and arsenious acids, (pages 332, 424), the quantity of the chlorine only which is contained in the volatile chlorides of these substances is determined.

#### SEPARATION OF CHLORINE FROM SULPHUR.

\* When the chlorides of sulphur are treated by water, a portion of the sulphur is separated, and renders the water

milky, whilst the other portion is converted into hyposulphurous acid, which undergoes a farther decomposition, being converted into sulphurous acid and sulphur. A long time must elapse, however, before the decomposition of the hyposulphurous acid is complete. If the operator wishes, by pouring a solution of nitrate of silver in the liquor filtered from the sulphur, to precipitate in the state of chloride of silver the muriatic acid contained therein, he generally obtains a brown precipitate, because, although the water may have been left to act for a long time upon the chloride of sulphur, the liquor still contains a little undecomposed hyposulphurous acid, which produces a precipitate of sulphuret of silver, mixed with the chloride of this metal. This mixture of chloride and of sulphuret of silver must then be digested for a long time in pure nitric acid of moderate strength, which oxydises the sulphuret of silver without attacking the chloride of silver. This method is better than that which consists in pouring ammonia upon the mixture whilst still moist, which would dissolve the chloride, and leave the sulphuret of silver; the chloride of silver might subsequently be precipitated from the ammoniacal solution by saturating it with an acid.

\* In such an analysis the quantity of the sulphur can be estimated only by the loss.

The quantity of the sulphur may be determined with much more precision than that of the chlorine in the chlorides of sulphur. The best method of doing it consists, after having weighed the chloride, as was said before, in introducing it in a bottle containing fuming nitric acid, and capable of being perfectly closed with a glass stopper. As soon as the glass bulb is broken, the chloride of sulphur dissolves in the acid with ease and rapidity, and ordinarily without leaving any sulphur, unless there is an excess of it. After having diluted the liquor with a suitable quantity of water, and left the whole in digestion for some time, the sulphur which has refused to

dissolve is collected on a filter, and solution of chloride of barium is poured in the filtered liquor to precipitate the sulphuric acid which has been produced by the experiment. From the quantity of the sulphate of baryta obtained, that of the sulphur is calculated. In this method the quantity of the chlorine contained in the chloride of sulphur is estimated from the loss, for the action of fuming nitric acid upon chloride of sulphur does not convert the whole of the chlorine into muriatic acid, and therefore it cannot be wholly precipitated in the state of chloride of silver, by a solution of nitrate of that metal.

#### SEPARATION OF CHLORINE FROM SELENIUM.

\* When the combinations of chlorine and selenium are dissolved in water, the result is the formation of muriatic acid, and selenious acid. If the experiment is performed upon chloride of selenium, (*chloride sélénieux*) a portion of the selenium is separated, whilst the other portion is converted into selenious acid. This selenium is left in digestion with the water for a long time, because it would otherwise retain a little chlorine also; it is then collected upon a weighed filter, and its quantity is determined. The filtered liquor contains muriatic and selenious acids. The former of these acids is to be first precipitated by solution of nitrate of silver; after having previously added some nitric acid to the solution, the supernatant liquor is immediately decanted from the precipitate. The operator should not use too great an excess of nitrate of silver, because, especially if the liquor is not very dilute, selenite of silver would be formed insoluble in water, and very sparingly soluble even in free nitric acid. Consequently, it is necessary to digest the precipitated chloride of silver in hot nitric acid, then with hot water, and to decant the liquor, which operation must be repeated, until the liquor ceases to become turbid by testing with muriatic acid. This elimination of all trace of selenite of silver from the chloride of silver requires a long time. In all these often repeated digestions with hot nitric acid, a little chloride of silver is unavoidably dissolved.

\* The first liquor which has been separated from the chloride of silver by decantation, often deposits after cooling and a prolonged rest, some crystallised selenite of silver, which is redissolved by washing, and especially by heating the solution, which may then be filtered. The excess of oxyde of silver is then precipitated by muriatic acid, and then the selenious acid is determined by the method described (page 363).

\* Selenite of silver being sparingly soluble, which renders it necessary to dilute largely the liquors which contain selenious acid, it is difficult to reduce the selenium without concentrating them by evaporation. If the operator possesses a sufficient quantity of the chloride to be analysed, it is advantageous to devote a fresh portion exclusively to the determination of the selenium.

\* The determination of the quantity of the chlorine by nitrate of silver being attended with some difficulties, on account of the formation of selenite of silver, the analysis may be conducted as follows:—The selenious acid is first precipitated from the aqueous solution by means of sulphuretted hydrogen, in the state of sulphuret of selenium (*sulfide sélénieux*), from which the selenium is determined, according to the method indicated (page 364). A solution of sulphate of protoxyde of copper is poured in the filtered liquor, in order to remove all trace of sulphuretted hydrogen, and the determination of the chlorine in the state of chloride of silver, by means of nitrate of silver, no longer presents any difficulty.

#### SEPARATION OF CHLORINE FROM TELLURIUM.

Perchloride of tellurium (*chloride tellurique*) is rendered milky by treatment with water, because tellurous acid is separated, a very small portion only of which is dissolved by the muriatic acid produced by the reaction of the water; if, however, a sufficient quantity of dilute sulphuric acid is added, the tellurous acid remains dissolved. By pouring a solution of

nitrate of silver in the liquor, the muriatic acid which has formed may be precipitated in the state of chloride of silver, and then, after having filtered the liquor, and removed by means of muriatic acid the excess of oxyde of silver employed, the tellurous acid may be determined therein by means of sulphite of ammonia.

\* The determination of the chlorine is not in that case attended with the same difficulties as for chloride of selenium (*chloride sélénieux*), because tellurite of silver is much more soluble in free acids than selenite of silver.

\* Protochloride of tellurium (*chlorure tellureux*) deposits, when treated by water, a precipitate of a grey colour, which is a compound of metallic tellurium, and of tellurous acid. If a sufficient quantity of dilute sulphuric acid is added to the water, there remains only metallic tellurium in a state of great division, and black, which is collected upon a weighed filter. The muriatic acid may be precipitated from the filtered liquor in the state of chloride of silver, by means of a solution of nitrate of silver, and after having removed the excess of oxyde of silver, the tellurous acid in solution is determined by means of sulphite of ammonia, which yields as much metallic tellurium as had separated in the metallic state at the beginning of the experiment.

#### SEPARATION OF CHLORINE FROM TITANIUM, TIN, AND ANTIMONY.

\* When to an aqueous solution of chloride of titanium, or of perchloride of tin, even after having acidified it by nitric acid, a solution of nitrate of silver is added, a precipitate of stannate or of titanate of silver, sparingly soluble in nitric acid, is produced along with chloride of silver. It is therefore necessary to pass a current of sulphuretted hydrogen through the solution of the perchloride of tin, in order to precipitate the peroxyde of tin in the state of persulphuret of tin. But as persulphuret of tin is not precipitated rapidly by sulphuretted hydrogen gas, and in a complete manner, only when left in digestion

with the reagent, which might volatilise traces of muriatic acid, the precipitation and digestion must be operated in a bottle capable of being closed. If the operator has the precaution to add a little dilute sulphuric acid to the solution, the sulphuret of tin is precipitated better, and the digestion in a closed flask may be dispensed with.

When after the lapse of a long time, all the sulphuret of tin has deposited, it is collected upon a filter, and it may be quantitatively determined as was said (page 270). This being done, the quantity of the chlorine in the filtered liquor is determined; but as the solution might still contain traces of sulphuretted hydrogen, these must be first eliminated, because otherwise, the precipitate of chloride of silver produced by the addition of nitrate of silver would be contaminated by sulphuret of that metal. Wherefore, after having separated the sulphuret of tin by filtering, a small quantity of sulphate of protoxyde of copper is added to the liquor, which destroys the sulphuretted hydrogen by producing a precipitate of sulphuret of copper, which is separated by filtering, and nitrate of silver is then added to the filtered liquor. From the quantity of chloride of silver precipitated, that of the chlorine which existed in the chloride submitted to analysis is determined.

The solution of chloride of titanium (*chlorure titanique*) in water is slightly milky; this is owing to a small quantity of titanac acid which has been liberated by the heat evolved during the mixture of the chloride with water. The titanac acid is first precipitated by ammonia, an excess of which should be avoided. The whole is then left at rest in a place moderately heated, until the odour of ammonia is no longer perceived, and the titanac acid is then collected on a filter. The filtered liquor is acidified by pouring a little nitric acid upon it, and the chlorine is then precipitated in the state of chloride of silver, by means of a solution of nitrate of that metal.

If perchloride of antimony had to be analysed, the operator

should add to the water used to decompose it a sufficient quantity of tartaric acid, that the solution may remain clear. The antimoniac acid is then precipitated in the state of sulphuret of antimony by means of a stream of sulphuretted hydrogen, and the sulphuret should be treated as was said (page 288). A little of a solution of protosulphate of copper is added to the filtered liquor to destroy the last traces of sulphuretted hydrogen, and after having separated the sulphuret of copper by filtering, the chlorine is precipitated by nitrate of silver.

The solution of chloride of antimony in muriatic acid (butter of antimony) is analysed in the same manner. In that case there is less danger of loss during the decomposition of the water, wherefore, the weighing and the dissolving in water may be performed in the usual way, without being fettered by any of the rules or precautions mentioned (page 574).

#### SEPARATION OF CHLORINE FROM MOLYBDENUM AND TUNGSTEN.

When muriatic acid has to be separated from molybdic acid in aqueous solutions of chloride of molybdenum, the analysis is attended with difficulties similar to those for the separation of muriatic acid from selenious acid (page 579), because molybdate of silver is very sparingly soluble even in hot nitric acid. The analysis is performed like that of chloride of selenium. The chloride of silver fused and weighed, should be fused with carbonate of soda. The melted mass is treated by water, and the reduced silver is collected on a filter. The filtered liquor is acidified with muriatic acid, and an aqueous solution of sulphuretted hydrogen is poured in, in order to ascertain whether it is free from molybdate of silver, which, if any was present, would produce a brown precipitate of sulphuret of molybdenum.

\* If the operator wishes at first to treat the aqueous solution of chloride of molybdenum by sulphuretted hydrogen, in order to determine the molybdic acid in the state of brown sulphuret of molybdenum, and then to separate the muriatic from the

filtered liquor in the state of chloride of silver, he encounters difficulties again, because it is difficult to precipitate the molybdic acid in the state of sulphuret of molybdenum. The process has been indicated (page 312). A solution of proto-sulphate of copper is added to the liquor filtered from the sulphuret of molybdenum, and the muriatic acid is then precipitated in the state of chloride of silver.

\* The separation of tungstic and of muriatic acids contained in the solution of chloride of tungsten is so difficult, that the operator must rest satisfied with determining the tungstic acid only, which is easily performed by saturating the solution of chloride of tungsten with ammonia, evaporating to dryness, and igniting the dry mass; that which remains is tungstic acid. If the operator were to acidify the ammoniacal solution of chloride of tungsten with nitric acid, the tungstic acid would not be completely precipitated; and if he were to add a solution of nitrate of silver to the filtrate, a precipitate consisting of a mixture of chloride and of tungstate of silver would be produced, which could not be separated from each other by nitric acid.

#### SEPARATION OF CHLORINE FROM CHROMIUM.

\* The solution of chloride of chromium must be rendered ammoniacal; after having treated the chloride by water, ammonia is added thereto, in order to prevent the formation of chlorine from the action of the free muriatic acid upon the chromic acid. The solution is then acidified by nitric acid, and a solution of nitrate of silver is added. Frequently, and especially when the liquor is not very dilute, chromate of silver is precipitated along with the chloride of this metal, which chloride of silver, though sparingly soluble, dissolves easily in dilute nitric acid and in hot water. With respect to the liquor filtered from the chlorine of silver, the excess of the oxyde of silver is precipitated by sulphuretted hydrogen, which reagent converts at the same time the chromic acid into oxyde of chromium, which may be precipitated by ammonia.



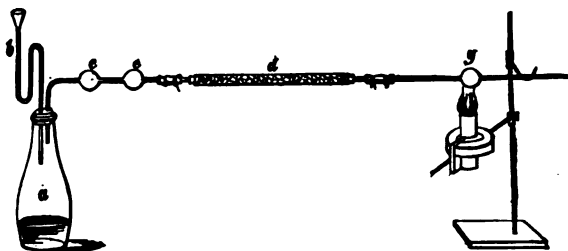
## DETERMINATION OF CHLORINE IN INSOLUBLE COMPOUNDS.

Some chlorides are insoluble in water, most of which dissolve however in acids. This is the case with several combinations of metallic chlorides with metallic oxydes. When a combination of this kind has to be submitted to analysis, it is dissolved in an acid, the solution is diluted with water, and a solution of silver is poured in it, in order to determine the muriatic acid from the chloride of silver precipitated, exactly as for the chlorides which are soluble in water. Nitric acid is the solvent generally employed for the purpose. When it can dissolve the combination in the cold its use is not objectionable, but if the application of heat is necessary to effect the solution, it may happen that a portion of the metal combined with the chlorine will be oxydised by the nitric acid, and a certain quantity of chlorine may be disengaged. This effect, however, occurs only in a very small number of cases, and especially when the chloride has been evaporated to dryness with a large excess of nitric acid, by which means a very great number of metallic chlorides may successfully be transformed into nitrates. If the combination has been dissolved by digestion in hot and dilute nitric acid in a flask closed with a glass stopper, and if, after perfectly cooling, the liquor be then diluted with water, and a solution of nitrate of silver poured into it, the whole of the chlorine will be obtained in the state of chloride of silver.

\* Some metallic chlorides which are insoluble in water are likewise insoluble in the dilute acids; such are for example, chloride of silver and subchloride of mercury. When the quantity of silver has to be determined in a small quantity of chloride of silver, the latter should be heated in an atmosphere of hydrogen gas, which produces metallic silver under disengagement of muriatic acid gas. This may be done by means of the apparatus described (page 138), and reproduced in the next page.

The chloride of silver is introduced into the bulb *g*, and weighed with it. The hydrogen gas is disengaged in the usual way. The chloride of silver is then converted into metallic silver at a temperature which needs not be very high. When muriatic

acid ceases to be evolved, which is recognised when white fumes are no longer produced by holding a glass rod moistened with ammonia at the orifice of the tube of the bulb *g*, the apparatus is allowed to cool, and the metallic silver is then weighed.



\* Most metallic chlorides, the oxydes of which are convertible into metal when heated in an atmosphere of hydrogen may be treated in the same manner. I shall remark here only that a stronger heat is required to reduce chlorides than is necessary for the oxydes. Yet, amongst the numerous metallic chlorides which are known, chloride of lead is about the only chloride which may be thus treated when, on account of its sparing solubility, the operator is unwilling to dissolve it in water; but when chloride of lead is reduced by hydrogen gas, the heat employed must be as moderate as possible, because at a high temperature some of the chloride of lead might be volatilised.

\* The quantity of the metal only is ordinarily determined by this process. That of the muriatic acid produced may be estimated also by receiving the gases which have passed over the metal into dilute ammonia, supersaturating the solution with nitric acid, and precipitating the muriatic acid by a solution of nitrate of silver. If, however, the hydrogen gas has not been passed very slowly over the combination, it may happen that a little muriatic acid will escape with the bubble of gas.

\* *Another method* may be employed to decompose the chloride of silver, and determine the quantity of the silver therein. It is

mixed in a small porcelain crucible with double its weight of carbonate of soda, or better still, with double its weight of a mixture of five parts of carbonate of potash and four parts of carbonate of soda; the whole is then heated upon an argand spirit-lamp. The silver is already reduced completely under disengagement of carbonic acid, long before the alkali has arrived to perfect fusion. When all effervescence has ceased, the crucible is allowed to cool, and the mass is treated by water; the silver remains in a very finely divided state; it is collected on a filter, washed, ignited, and weighed.

\* This method is resorted to with great advantage when it is not necessary to introduce the chloride in a glass bulb, and more especially when, in an analysis, the chloride of silver obtained having been fused and then weighed in a porcelain crucible, the operator wishes to determine whether it is perfectly pure. It is then mixed with carbonate of alkali, the whole is ignited, and from the quantity of silver obtained it is easy to see whether the chloride of silver operated upon was pure, and corresponds with the calculation.

Chloride of silver may, however, be analysed by a *third method*. After having fused it, a piece of iron or of pure zinc is placed upon it, and water is poured upon the whole; after some time chloride of iron or of zinc is formed, which remains in solution, and the chloride of silver is converted into metallic silver. A few drops of dilute sulphuric acid hasten the reduction, and prevent the precipitation of peroxyde of iron from the decomposition which the protochloride of iron would undergo from the influence of the air. The chloride of silver which is not fused, but is in a state of great division in water, is treated in the same manner, that is to say, a bright strip of iron or of zinc is put in the mixture. After its reduction, the silver separated from the excess of zinc or iron may be washed and weighed; the liquor is acidified by nitric acid, and by means of nitrate of silver the chlorine may be precipitated from the solution in the state of chloride of silver.

*Subchloride of mercury* may be decomposed simply by digesting it in a solution of pure potash. The liquor filtered from the suboxyde of mercury contains the chlorine in the state of chloride of potassium. The solution is acidified by means of nitric acid, and a solution of nitrate of silver is poured therein in order to precipitate the mercury in the state of chloride of silver. The mercury contained in the suboxyde of mercury obtained might be estimated by various methods, but it is better to operate upon a fresh quantity of *subchloride of mercury*, reduced into powder, and to treat it by muriatic acid, and by a solution of phosphorous acid, in order to determine the quantity of metallic mercury, by the process which has been described (page 209).

#### DECOMPOSITION OF CHLORIDES BY SULPHURETTED HYDROGEN.

Several of the combinations, insoluble in water and in acids, which chlorine forms with the metals which sulphuretted hydrogen precipitates completely from their solutions in the state of metallic sulphurets, may be analysed in the following manner:—A certain portion of the compound is reduced into fine powder and weighed; it is mixed with water in a bottle capable of being closed, and a current of sulphuretted hydrogen is passed through the mixture to supersaturation. The metal is thereby converted into metallic sulphuret, and the chlorine into muriatic acid, which remains in solution. The metallic sulphuret is collected on a filter, and a solution of protosulphate of copper is added to the liquor, which, by reason of the sulphuretted hydrogen in the solution, produces a precipitate of sulphuret of copper. This sulphuret is separated by filtering, and the chlorine is then precipitated from the filtered liquor by means of a solution of nitrate of silver. The composition of the substance may then be estimated from the metallic sulphuret, and the chloride of silver obtained.

It is necessary in this operation, after having passed sulphuretted hydrogen through the mixture for some time, to shake the

mixture well, in order to bring all the parts of the pulverised compound in contact with the gas. The operator knows that no more gas is absorbed when, after having shaken the mixture for some time, it has yet a strong odour of the gas.

DECOMPOSITION OF CHLORIDES BY HYDROSULPHURET OF  
AMMONIA OR SULPHURET OF BARIUM.

The chlorides which are insoluble in water may be analysed by another method still, which is applicable also to those, the metals of which cannot be precipitated completely from neutral solutions in the state of metallic sulphurets by soluble sulphurets, which is the case with manganese, iron, zinc, and cobalt. A certain quantity of the chloride to be analysed is weighed, and hydrosulphuret of ammonia, or a solution of sulphuret of barium, or some other soluble sulphuret, is poured upon it. It is best to perform this experiment in a bottle capable of being closed, because the whole may be then digested by a very gentle heat. After having separated by filtering the metallic sulphuret which has precipitated, the filtered liquor which contains muriate of ammonia, or chloride of barium, together with the excess of hydrosulphuret of ammonia, or of sulphuret of barium employed, is decomposed by carefully pouring dilute sulphuric acid into it, and protosulphate of copper is then added in order to get rid of all the sulphuretted hydrogen which exists in solution therein. After filtering, the chloride of silver is precipitated by means of a solution of nitrate of silver, and from the weight of the precipitate, the quantity of chlorine contained in the substance submitted to analysis is estimated.

DECOMPOSITION OF CHLORIDES BY SULPHURIC ACID.

Most of the non-volatile chlorides may be treated, in the dry state, like the fluorides, by concentrated sulphuric acid, which disengages the chlorine in the state of muriatic acid gas, after which the quantity of the metal which was combined with the

chlorine is calculated from that of the sulphate obtained; that of the chlorine is estimated from the loss. A very great number of these metallic chlorides cannot be decomposed by sulphuric acid, except with the help of heat; others altogether resist its action; lastly, some of them are decomposed by it, in such a manner, that this process cannot be employed to determine the quantity of the metal combined with the chlorine. Perchloride of mercury is not decomposed by sulphuric acid, even with the help of heat. Subchloride of mercury is converted by this acid into perchloride and persulphate of mercury, under a disengagement of sulphurous acid. When chloride of gold is treated by hot sulphuric acid, metallic gold is reduced under a disengagement of chlorine and of muriatic acid gas; protochloride of tin deoxydises sulphuric acid. The other chlorides which are most often met with are more or less easily converted into sulphates by sulphuric acid, under disengagement of muriatic acid gas. Chloride of silver is, perhaps, that which is thus transformed with most difficulty; it is only by treating it repeatedly by hot sulphuric acid that it is ultimately converted into sulphate of silver.<sup>1</sup>

#### SEPARATION OF THE VOLATILE FROM THE NON-VOLATILE METALLIC CHLORIDES.

\* Several volatile metallic chlorides form with the chlorides of the metals the oxydes of which are powerful bases, double combinations, in which the operator does not always succeed in separating the chlorides which are volatile from those which are not so. Bonsdorff resorted to the following method to analyse the double salts which perchloride of mercury forms with the metallic chlorides:—The apparatus employed by him was very simple, and consisted of a small flask made out of a glass tube half an inch in diameter. This flask was six inches long, had a bulb at one of its extremities, and a globular swelling blown a

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<sup>1</sup> This method is more particularly applicable to the chlorides of ammonia, of potash, of soda, of lime, of magnesia, of strontia, and of baryta.—Ed.

little above it; its open extremity was drawn out to a point of about 1-4th of an inch in the bore.

\* The analysis was performed in the following manner, which, when conducted with care, yields accurate results :—The combination was first introduced into the counterpoised apparatus, and, after having determined the weight of the compound, the apparatus was closed with a cork, but not air-tight. The bulb was first gently heated with the lamp, in order to expel the water of crystallisation which collected in the upper part of the apparatus, the swelling above alluded to prevented it from falling back into the flask. This water was then removed with blotting-paper, or volatilised by a gentle heat. After this nothing remained, or at most only a scarcely distinguishable layer of perchloride of mercury at the lower part of the flask. After having closed the orifice with a cork, the bulb was again heated in order to expel the water which remained, and which was driven likewise into the upper part. By weighing the apparatus when cold, the weight of the water contained in the combination was thus arrived at. The cork was then replaced as before, and by increasing the heat the perchloride of mercury was sublimed, most of which collected in the swelling above spoken of. It was never discovered, by weighing again the apparatus when cold, that a single particle of the sublimate had been lost. By cutting the tube between the bulb and the flask the two metallic chlorides may be separated and respectively weighed. As, however, the perchloride of mercury may still contain a few milligrammes of water, it is advisable to dry it over concentrated sulphuric acid. When the metallic chloride which remains can support a red heat without being altered, it is ignited in the bulb which was cut off from the flask. By weighing it before and after, the operator ascertained whether it contained still or not a small quantity of perchloride of mercury.

#### SEPARATION OF CHLORINE FROM CARBON.

\* The combinations of chlorine with carbon, which are insoluble in water are analysed in quite a different way. A

small quantity of the combination is weighed and treated by protoxyde of copper in the manner described Chapter LIII.; the quantity of the carbonic acid formed is determined, from which that of the carbon is calculated; the loss indicates that of the chlorine.

\* The metallic chlorides are contained often in considerable, but sometimes, also, in very slight quantities, in other native combinations, for example, in fluorides, arseniates, phosphates, carbonates, and silicates.

#### SEPARATION OF CHLORINE IN SILICIOUS COMPOUNDS.

When silicates contain metallic chlorides, and are capable of being decomposed by acids, they are treated by cold nitric acid. If the combination cannot be decomposed by acids, except with the help of heat, it must be digested with these acids in a bottle provided with a glass stopper. The silicic acid liberated is then separated by filtering, and a solution of nitrate of silver is poured in the filtered liquor, in order to separate the chlorine. After having collected upon a filter the chloride of silver produced, the excess of oxyde of silver is precipitated by means of muriatic acid; the quantity of the other bases, if any, may afterwards be determined by the methods which have been described before. The compounds of this kind found in nature are sodalite, eudialite, and pyrosmalite<sup>1</sup>.

If the silicious compounds which contain metallic chlorides cannot be decomposed by acids, they must be ignited with

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<sup>1</sup> Sodalite is a combination of soda, silica, and alumina, with some muriatic acid. A sample of sodalite from Vesuvius, analysed by Berzelius and Wachtmeister gave,

Soda	.	.	.	.	.	.	20.96
Silica	.	.	.	.	.	.	50.98
Alumina	.	.	.	.	.	.	27.64
Muriatic Acid	!	.	.	.	.	.	1.29
							100.87

Another sample of sodalite from Litchfield (Maine, United States), in small



carbonate of alkali. The ignited mass is treated by water which dissolves the excess of carbonate of alkali and the chloride of sodium or of potassium produced. The solution is saturated by nitric acid, and the chlorine is precipitated therefrom by solution of nitrate of silver.

SEPARATION OF CHLORINE FROM FLUORIDES, ARSENIATES,  
PHOSPHATES, AND CARBONATES.

In order to analyse the fluorides, arseniates, phosphates, and carbonates which contain metallic chlorides, a certain quantity thereof is weighed, and, if practicable, dissolved in nitric acid; the liquor is then diluted by water, and a solution of nitrate of silver is poured into it. In order to determine the chlorine in all these combinations, it is advisable to operate separately upon a known weight of the compound. The fluorides must be dissolved in a platinum vessel, in which they are diluted with water, and the chloride of silver is precipitated by solution of nitrate of that base. When the quantity of the fluoride is very

crystalline masses of a fine blue colour, was analysed by Mr. Whitney of Boston, in H. Rose's laboratory, and that chemist gives the following results :—

				CALCULATED.
Silica	. . . . .	37.30	. . . . .	37.63 . . . . . 37.60
Alumina	}	32.88	. . . . .	{ 30.93 . . . . . 31.57
Peroxyde of iron				
Soda	. . . . .	23.86	. . . . .	25.48 . . . . . 25.47
Potash	. . . . .	0.59		
Chlorine	. . . . .	6.97		7.21

Which agrees with the composition established by M. de Kobell,



The composition of eudialite has been given before.

Pyrosmalite, according to Hisenger, contains

Silica	. . . . .	35.850
Chlorine	. . . . .	3.760
Protoxyde of iron	. . . . .	35.480
Sesquioxycde of manganese	. . . . .	23.444
Lime	. . . . .	1.210
Water	. . . . .	3.600
		103.344

slight, the combinations may be decomposed also in a glass vessel. If this combination contain only a very small proportion of metallic chloride, but a large quantity of phosphoric acid exists simultaneously in it, so that the latter cannot be quantitatively determined with great accuracy, it is impossible to determine immediately the quantity of the fluorine, which is the case amongst other compounds, with several varieties of apatite. Two portions of the combinations are then devoted to the determination of the chlorine and of the bases which are combined in the state of oxydes with the phosphoric acid, or in the state of metal with the fluorine or chlorine. Another portion of the combination is afterwards ignited with an excess of carbonate of soda, and the fused mass is afterwards treated by water, by which means a solution of phosphate of soda, and of fluoride of sodium is obtained which may be analysed, as was said (page 567).

DETERMINATION OF CHLORIC AND OF PERCHLORIC ACID IN  
THEIR COMBINATIONS.

Respecting the degrees of oxydisation of chlorine and of their combinations with bases, it is often very difficult to analyse such compounds. In order to determine, in chlorates and oxychlorates, the quantity of chlorine contained in the acid, and that of the metal which exists in the oxyde, it is best to submit a weighed quantity of the salt to a prolonged ignition. The salt is thereby converted into metallic chloride, whilst oxygen gas is disengaged. If the salt contains no water of crystallisation, its composition may be easily calculated from the quantity of metallic chloride obtained; that of the chloric acid might also be determined from the volume of oxygen gas disengaged.

\* The chloric acid contained in solutions may be transformed by several reducing substances, such as, for example, sulphuretted hydrogen, into muriatic acid, in which, after having destroyed the excess of sulphuretted hydrogen by a solution of protosulphate of copper, the chlorine may be determined by

means of nitrate of silver in the state of chloride of silver, which may serve to calculate the quantity of the chloric acid.

\* As to perchloric acid, this substance might, in a great number of cases, be separated from other substances in the state of perchlorate of potash, (page 9).

#### DETERMINATION OF CHLOROUS ACID IN CHLORITES.

The analysis of the chlorites is more important in a technical point of view. It very often happens that the operator has to analyse solutions of chlorites of soda and of potash, mixed with chloride of sodium and chloride of potassium, but more particularly still, solutions of chlorite of lime mixed with chloride of calcium and hydrate of lime, which combination is ordinarily called chloride of lime, all of which substances are largely employed for bleaching, and as purifying agents. It is consequently important to ascertain the quantity of chlorine which they disengage when treated by acids. With respect to the analysis of chloride of lime, or rather the determination of the quantity of chlorine evolved from any given weight of chloride of lime when put in contact with acids, Gay Lussac has indicated a method which answers all commercial or technical purposes. It consists in triturating a weighed quantity of chloride of lime with a certain known quantity of water, and to use it for decolorising a given proportion of a sulphuric acid solution of indigo. The greater or less quantity of indigo decolorised indicates the quantity of chlorine which the sulphuric acid of that solution disengages from the chloride of lime. If, however, the experiment is not performed with the necessary caution, this method often yields inaccurate results. In effect, the solution of indigo diluted with water, undergoes a change by keeping; sometimes, also, a little chlorine may be lost, which is disengaged by the sulphuric acid before it (the chlorine) has had time to act on the solution of indigo. This takes place when the liquids are mixed together too slowly, and the

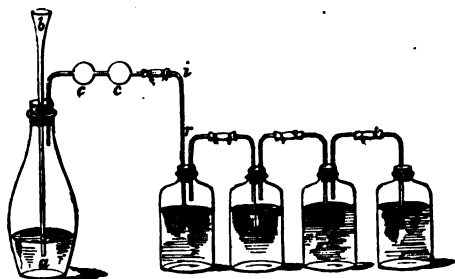
accuracy of the result depends, therefore, a great deal upon the rapidity with which the two liquors are mixed together.

To obviate this, Marezeau proposed another method for the determination, for a technical purpose, of the quantity of chlorine which acids disengage from chloride of lime. His method consists in triturating a given weight of this substance, with a known weight of water, and carefully pouring the mixture little by little into a dilute solution of subnitrate of mercury of a known strength, and to which an excess of dilute muriatic acid has been added. The operator continues to do so until the precipitate of subchloride of mercury produced by the muriatic acid, has entirely disappeared. The subchloride of mercury, the quantity of which is known from that of the solution of the subnitrate of mercury, requires as much chlorine as it already contains, to become converted into perchloride of mercury, and therefore, to dissolve in the water.

\* Gay Lussac has more lately made several improvements to the methods of analysing chloride of lime, and besides those which consist in the use of solution of indigo, and that of subnitrate of mercury, he proposed two other reagents, namely, arsenious acid, and ferrocyanide of potassium, the solutions of both of which have the advantage of undergoing no alteration, and may therefore be kept for a long time. The reader is referred for the description of these new methods to the 60th volume of the "*Annales de Chimie*."

When the chloride of lime consists only of chlorite of lime mixed with the quantity of chloride of calcium, which must be produced during its preparation, the most accurate method of determining, for scientific purposes, the quantity of chlorine, which acids disengage from it, consists in weighing a given quantity of it, decomposing it by dilute sulphuric acid, in a suitable apparatus, and passing the liberated chlorine gas into dilute ammonia. The ammonia is afterwards supersaturated by nitric acid, and a solution of nitrate of silver is added thereto,

which precipitates all the chlorine in the state of chloride of silver. An apparatus similar to that described (page 386) may be used for the purpose ;



but it is not necessary to put so many bottles containing ammonia in communication with the disengagement flask. A solution of carbonate of ammonia may likewise be employed, in order to produce a disengagement of carbonic acid, for the purpose of driving the last portion of chlorine of the apparatus into the bottles containing ammonia, and the operator must take care that the disengagement flask always contains an excess of sulphuric acid.

This method of analysis cannot be employed, however, when the chloride of lime contains chlorate of lime ; this is very often the case when the application of heat has not been carefully avoided during the preparations of the chloride, and when the hydrate of lime has been treated by an excess of chlorine.

#### SEPARATION OF CHLORATES AND PERCHLORATES FROM CHLORIDES.

When a liquor contains simultaneously a chlorate or a perchlorate and a chloride, and the quantity of each of the two bodies has to be separated, it may be easily done, provided a chlorite be not present at the same time. If the solution does not contain any free base, a solution of nitrate of silver is added to the liquor, by which the chlorine of the chloride only is

precipitated in the state of chloride of silver, from which the quantity contained in the chloride in question can then be easily calculated. By evaporating afterwards another portion of the liquor to dryness, igniting the residuum, redissolving it in water or in very dilute nitric acid, and pouring a solution of nitrate of silver in the solution, the chlorine of both the chlorate and the chloride is precipitated in the state of chloride of silver. It then suffices to determine the quantity of chlorine contained in the chloride of silver, and to deduct therefrom that which has been ascertained before as belonging to the chloride; the difference shows the quantity of chlorine contained in the chlorate, from which the proportion of chloric acid is then easily calculated.<sup>1</sup>

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<sup>1</sup> M. Köne (Pogg. Annal. LXIV. page 404,) proposed to separate chlorine from muriatic acid, when mixed together, by means of sulphate of potash, which is decomposed by muriatic acid into chloride of potassium, and into bisulphate of potash. Sulphate of potash is to be dissolved in the liquor, the chlorine is evaporated in the air, and in the dark, and the muriatic acid is precipitated afterwards by a salt of silver.—Ed.

## CHAPTER L.

## BROMINE.

## DETERMINATION OF BROMINE.

\* BROMINE may be determined in its combinations with metals exactly in the same manner as chlorine (page 572), by means of a solution of nitrate of silver. If the combination is soluble in water, it is treated exactly as that of the corresponding chlorides; the bromide of silver produced is separated precisely as chloride of silver. It is then dried, fused like the chloride, and from its weight that of the bromine is calculated.

\* Bromine is also determined in the volatile bromides exactly as in the volatile chlorides (page 574); the volatile bromides are less so than the corresponding chlorides.

\* The bromine of the insoluble bromides is separated by the same processes as the chlorine of the insoluble chlorides.

\* The separation of the volatile bromides from those which are not volatile, is effected in the same manner as those of the corresponding chlorides (page 585).

Bromides may also, like chlorides, be decomposed by sulphuric acid; the quantity of the bromine is then calculated from that of the sulphate obtained (page 587).

As the decomposition of the metallic bromides by sulphuric acid is attended with a disengagement of hydrobromic acid

gas, sulphurous acid gas and bromine, the experiment must be performed, not in a platinum crucible, but in a capsula or crucible of porcelain.

\* Several bromides, however, for example, bromide of mercury, are not decomposed by sulphuric acid.

\* When the quantity of free bromine has to be determined, the operation is the same as for the determination of free chlorine (page 572). Whether the bromine is pure, mixed or dissolved in water, it is to be carefully treated by an excess of ammonia which converts it completely into hydrobromate of ammonia, (*bromure ammonique*), under disengagement of nitrogen. The reaction is so strong, that if due care is not taken, a little hydrobromate may easily be volatilised. After having diluted the solution by a sufficient quantity of water, it is acidified with nitric acid, and by means of a solution of nitrate of silver, the bromine is precipitated in the state of bromide of silver.

#### SEPARATION OF BROMINE FROM CHLORINE.

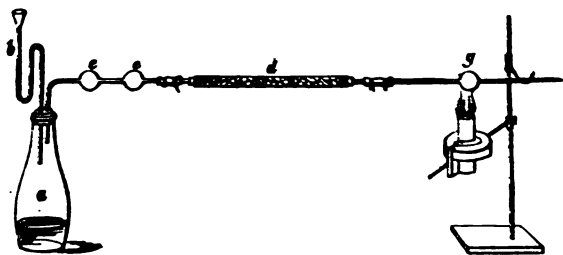
\* From that which has been said, it may be perceived that bromine can easily be determined with great accuracy from its combinations, when these are pure and unmixed with other compounds, but this determination is much less important than that which must be effected when the bromides are associated with chlorides, which is generally the case.

\* Chlorine and bromine, and the corresponding chlorides and bromides have so much analogy, that no exact method of separating bromine from chlorine is yet known. The determination of bromine is on that account performed generally in an indirect manner.

When the combination of bromine is associated to a chloride, the determination of the bromine may be effected in the



following manner, which is accurate:—The chlorine and the bromine are simultaneously precipitated from the liquor in the state of chloride and bromide of silver, by means of a solution of nitrate of silver, with the usual precautions. The precipitate is then dried and fused in the usual manner, and its weight is determined. As much of the fused mass as possible is removed from the porcelain crucible by moderately heating it, which slightly fuses the combination of silver on the sides, and allows of the greatest portion of it to be withdrawn by means of a glass rod. A weighed quantity of this is introduced into a glass bulb through which dry chlorine gas is passed, whilst it is heated. The bromine is thus expelled, and the whole of the combination of silver is converted thereby into chloride of silver the weight of which is less than that of the mixture of bromide and of chloride of silver operated upon. When the operator does not wish to collect the bromine, the following apparatus may be



used. The difference of weight between the mixture of bromide and of chloride, and of the pure chloride, must be multiplied by 1.826, in order to obtain the quantity of the bromine which was expelled from the mixture by the chlorine gas. The calculation is grounded upon this, namely: that the quantity of the bromine is to this difference of weight as the atomic weight of bromine and of chlorine. The quantity of the chlorine is found by deducting from the mixture of chloride and of bromide of silver the quantity of silver which exists in the chloride of silver obtained in the last instance, which indicates the collective weight of the chlorine and of the bromine, from which the calculated quantity of the bromine must be subtracted.

\* According to Berzelius, this method may be practised inversely and yet retain its accuracy. After having fused the mixture of bromide and of chloride of silver in a porcelain crucible, it is reduced by placing upon it a small piece of distilled zinc, or of pure iron ; at the end of twenty-four hours, the reduction is complete. The liquor is acidified with a drop of muriatic acid. The reduced silver may then be perfectly detached from the crucible ; it must be crushed to pieces, and boiled first with acidified water, and then with pure water ; it is subsequently ignited, and weighed. The operator afterwards calculates how much chlorine is required to convert this silver into chloride, the difference between the latter and that of the mixture of the chloride and bromide is ascertained, and the calculation is resumed as above.

Berzelius indicated *another method* of separating chlorine from bromine, and immediately determining the latter. In this method, when the chlorine and bromine are contained in the compound under examination with metal or with hydrogen, it is necessary to separate them from these other bodies, and so that they may be in a free state. For this purpose the combination is mixed with peroxyde of manganese, in a small tubulated retort provided with a receiver containing a little water. An excess of sulphuric acid previously diluted with one-fifth of water is poured in the retort, and heat is applied. The chloride of bromine (into which one or the other of the two constituents predominates more or less) condenses in the receiver, which must be kept quite cool, and dissolves in the water contained in this receiver. When reddish vapours cease to be produced, it is a sign that the operation is at an end. The aqueous solution of bromine containing chlorine is then completely saturated by gaseous chlorine, and hydrate of potash is added until the liquor becomes colourless. There is formation of chloride of potassium, of chlorate, and of bromate of potash. Nitrate of silver is then poured in the liquor, which produces a precipitate of chloride and of bromide of silver. After

having washed the precipitate, it is macerated with baryta-water in a closed flask, by which bromate of silver is produced whilst the chloride of silver is not decomposed. The baryta-water, an excess of which must have been employed, having been evaporated, crystallised bromate of baryta is obtained, which must be washed with a little spirits of wine, in order to be certain that it contains no trace of chloride of barium, after which it is converted into bromide of barium by ignition.

The French edition has the following remarks by E. Peligot:—

\* None of these methods, but more especially the first of them, can be employed to determine even approximatively small quantities of bromide when mixed with larger quantities of chlorides. And yet this case is of most frequent occurrence; bromine existing only in salt water, and certain mineral waters in which it is found, only in very slight proportion comparatively to the quantity of the chlorides.

\* When the operator has a great quantity of such waters, it is possible to concentrate the bromine contained in them sufficiently to be able to determine it with certainty. To a given weight or volume of the water a solution of nitrate of silver is added, which precipitates together the chlorine and the bromine in the state of chloride and of bromide of silver, the weight of which may then be determined. If the water is alkaline, it is previously acidified by nitric acid; nitrate of silver is afterwards carefully added to another somewhat considerable volume or weight of the water, so as to precipitate not the whole, but only the greatest part of the chlorine: the chloride of silver is collected on a filter, and its weight is determined. So long as the whole of the chlorine is not precipitated, all the bromine is still in solution. If afterwards more nitrate of silver is added to the filtered liquor, taking care to pour an excess of it towards the end, the remainder of the chlorine and the whole of the bromine are precipitated in

combination with the silver, and the quantity of bromine in the precipitate may be so great, compared with that of the chlorine, that the preceding method of determining the bromine possibly may be employed for that purpose. That method, it will be recollected, consists in converting the whole of the combinations of silver into pure chloride of silver by means of chlorine gas.

\* *Another method* of separating bromine from chlorine has been proposed by Mr. Henry, which consists in precipitating these two bodies in the state of bromide and of chloride by means of nitrate of silver, the precipitate is then put in contact with dilute sulphuric acid and zinc. When the reduction of the silver is completed, the liquor is filtered, and a slight excess of baryta is added to it; the liquor is again filtered, and the filtrate is evaporated to dryness; it consists of chloride and of bromide of baryta, mixed with the excess of baryta; this residuum is then treated by absolute alcohol which dissolves the bromide of barium only.

According to M. Piria the following process may likewise be employed:—The mixture of chloride and of bromide is decomposed in a retort by weak sulphuric acid, the muriatic and hydrobromic acids are collected in a solution of caustic baryta the excess of which is afterwards precipitated, when the disengagement of the above acids has ceased, by a current of carbonic acid. The liquor being filtered, it is evaporated to dryness, and treated by absolute alcohol which dissolves the bromide and leaves the chloride of barium.

\* In either process the salt obtained should be decomposed by an acid solution of nitrate of silver, in order to estimate the bromine in the state of bromide of silver.

## DETERMINATION OF BROMIC ACID.

\* Bromic acid may be determined in many of its combinations by a process analogous to that which is employed for the determination of chloric acid (page 594). When the bromates are ignited, they are converted, under disengagement of oxygen gas, into metallic bromides, in which the bromine can be determined in the usual manner.

\* Bromic acid might, perhaps, be separated in certain cases as bromate of silver, which, like chloride of silver, is soluble in ammonia, and insoluble in dilute nitric acid.

## CHAPTER LI.

## IODINE.

—♦—  
DETERMINATION OF IODINE.

\* IODINE may also be determined in its soluble combinations with metals and with hydrogen in the same manner as chlorine and bromine, namely, by means of nitrate of silver. If the liquor contains carbonates, it is advisable to acidify it by nitric acid, not, however, before adding nitrate of silver to it but afterwards, otherwise some iodine might be separated, which would not be completely converted into iodide of silver by solution of silver.

\* After having dried the iodide of silver, it is treated in the same manner as the chloride of silver.

\* If the combinations which contain iodine are insoluble, they must be decomposed by carbonate of potash or of soda, by sulphuretted hydrogen, or by hydrosulphuret of ammonia, as the corresponding chlorides (pages 585, 588, 589).

Most iodides can be decomposed by sulphuric acid, and transformed into sulphates in the same manner as for the chlorides, (page 589). As this decomposition produces a disengagement of sulphurous acid and of iodine, vessels of platinum must not be used. From the quantity of sulphate obtained,

## SEPARATION OF IODINE FROM BROMINE.

\* When the combinations which contain these two substances are soluble, they may be separated from each other, by the same methods which are employed for separating iodine from chlorine, a solution of nitrate of silver is poured in the liquor, in order to precipitate simultaneously the bromide and iodide of silver, which two bodies are afterwards separated from each other by ammonia. This experiment yields more accurate results than those which are obtained in separating chloride from iodide of silver in the same manner, because bromide of silver is less soluble in ammonia than chloride of silver.

\* We have seen (pages 601, 606), that chlorine gas may be employed to convert a mixture of chloride and of bromide, or of chloride and iodide of silver, into chloride of silver, from the weight of which, that of the bromine, or of the iodine, may be determined; the same method is applicable to a mixture of bromide and iodide of silver, which may thus be converted into bromide of silver, by the fumes of bromine. The calculation is absolutely identical in both cases.<sup>1</sup>

## DETERMINATION OF IODIC ACID AND OF OXYIODIC ACID.

\* Under the influence of heat, many of the combinations of these acids may be converted, under disengagement of oxygen gas, into metallic iodides, in which the quantity of iodine may be easily determined. In the oxyiodates, the excess of iodic acid is volatilised under the form of iodine, and of oxygen. It is

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mixture of an iodide and of a chloride, the precipitate produced may indicate exactly the quantity of iodine. In order to identify the precipitate, it should be separated, dissolved in ammonia, and a few drops of a recently-prepared solution of starch should be poured in, and an excess of sulphuric acid being added, should impart immediately a blue colour to the liquor.—Ed.

<sup>1</sup> That is to say, the quantity of the iodine is to the difference of the weights obtained, as the equivalent of iodine (1578.29) is to the difference between the equivalent of bromine and that of iodine (600.1). The operator multiplies then the difference found by 2.630, which is the quotient of 1578.89, divided by 600.1.—Ed.

necessary to remark, that sometimes when an iodate is submitted to heat, and this salt is already converted into an iodide, the latter may lose a little iodide during ignition, as is the case amongst others with iodide of sodium. Iodate of soda requires a white heat to become converted into iodide.

\* The bases contained in iodates are more accurately determined, when they are capable of being precipitated by either sulphuretted hydrogen, hydrosulphuret of ammonia, or carbonate of alkali. Iodates may likewise be decomposed by sulphuric acid, and thus converted into sulphates, from the weight of which the composition of the iodates is calculated.

\* In certain cases, oxyiodic acid might be separated in the state of a salt of silver, by solution of nitrate of silver.



## CHAPTER LII.

## NITROGEN.

## DETERMINATION OF NITROGEN.

THE quantitative determination of nitrogen in the state of gas, occurs only in cases when it has to be separated from other gases. Ordinarily the operator absorbs the other gases by which it may be accompanied, by different reagents, after which its volume is determined. The precautions to be observed in performing this experiment will be developed in the ensuing chapter.

## DETERMINATION OF NITRIC ACID.

OF all the degrees of oxydisation of nitrogen, the most important is unquestionably nitric acid. The quantitative determination of this acid is, in many instances, attended with difficulties. When it exists in a liquor which contains no other acid besides, it may be very accurately determined in the following manner:—Solution of hydrate of baryta [baryta-water] is added to the liquor until it renders reddened litmus paper blue. Ordinarily, the excess of baryta thus added is removed by passing a current of carbonic acid through the solution, which produces a precipitate of carbonate of baryta, a slight quantity of which is kept in solution by the excess of carbonic acid, wherefore the solution, after having thus been submitted to a stream of carbonic acid gas, must be boiled. The carbonate of baryta produced is afterwards separated by filtering; the

filtrate contains nitrate of baryta. It is carefully evaporated to dryness at a gentle heat, and from the weight of the dry salt, that of the nitric acid is calculated.

It is better, however, to operate as follows:—To the liquor containing nitric acid, add a sufficient quantity of hydrate of baryta, taking care not to put too much of it;<sup>1</sup> it is then evaporated slowly to dryness, without previously precipitating the excess of baryta by carbonic acid. The baryta is completely converted into carbonate by the carbonic acid of the air, provided too large an excess of hydrate of baryta has not been employed. Water is then poured upon the dry mass, and the carbonate of baryta is collected and filtered. The filtered liquor, which is a solution of nitrate of baryta, may then be evaporated to dryness, and from the weight of this salt, left as a residuum, the quantity of the nitric acid may be determined; but it is better to precipitate the baryta from the solution by adding dilute sulphuric acid thereto. In that case the operator must have ascertained that the liquor contains no longer any trace of hydrate of baryta. The quantity of nitrate of baryta or of nitric acid is subsequently calculated, by means of the tables, from the weight of sulphate of baryta obtained.

\* In evaporating the liquor which contains the nitrate of baryta in solution, the operator must take care not to heat too much towards the end, for fear of destroying a portion of the nitric acid.

\* Carbonate of baryta may be used in this analysis instead of hydrate of baryta, but the latter is preferable.

\* *Another method* may also be employed for the determination of nitric acid in a solution; a weighed quantity of protoxyde of lead is added to the solution, and the whole is

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<sup>1</sup> Hydrate of baryta must be added until the liquor begins to have an alkaline reaction.—ED.

evaporated to dryness. The mass which has thus been carefully dried is weighed, and it indicates the quantity of the nitric acid. This method, however, does not give results so accurate as that which consists in determining nitric acid by means of baryta. This acid forms with protoxyde of lead several basic salts, which are insoluble in water, and which, consequently, cannot be well separated from the small proportions of carbonate of lead which during the evaporation may have been produced at the expense of the excess of oxyde of lead employed. With baryta, on the contrary, nitric acid produces no basic salts, but a neutral salt only, which is soluble in water.

#### SEPARATION OF NITRIC ACID FROM THE BASES.

When nitric acid is combined with bases the nitrates are decomposed by sulphuric acid in a platinum crucible, and the nitric acid as well as the excess of sulphuric acid, is volatilised at an incipient red heat. The quantity of the base is afterwards calculated from the weight of the sulphate obtained, and the loss indicates that of the nitric acid. In operating thus, the sulphate must be of such a nature as not to lose its acid by ignition.

When the nitrates are ignited, they leave generally their oxyde in the pure state after the ignition, the loss indicates then the quantity of nitric acid, when the salt contains no water of crystallisation. The combination of nitric acid with the oxydes of the metals properly so called, do not require so great a heat to be converted into oxydes as those with the alkalies and alkaline earths; the latter require a very violent heat for their decomposition, and when the experiment is performed in the air, the liberated bases promptly absorb carbonic acid.

*Another method*, however, may be resorted to for separating the bases from nitric acid and then, in certain cases, the latter may be immediately determined. When nitric acid is combined with a metallic oxyde, with which it forms a salt soluble in water, and if the oxyde can be completely precipitated from the



solution of the salt in the state of metallic sulphuret, by means of sulphuretted hydrogen, the latter reagent is used to separate the base from the acid. The liquor filtered from the metallic sulphuret contains then the whole of the nitric acid, and also a little sulphuretted hydrogen in solution, an excess of solution of hydrate of baryta is poured in, and the operator proceeds exactly as was said above. In evaporating the whole to dryness, the excess of baryta combines with carbonic acid, and, at the same time, the small quantity of sulphuret of barium, produced by the sulphuretted hydrogen in solution, is transformed during the ignition into hyposulphite and sulphate of baryta. When water is afterwards poured upon the dry mass, the nitrate of baryta only is dissolved; sulphuric acid is then added to the solution, and from the weight of the sulphate of baryta obtained, the quantity of the nitric acid is calculated.

\* In this experiment it is necessary not to use too large a proportion of sulphuretted hydrogen to separate the metallic oxyde, as small an excess of the gas as possible being quite sufficient. The solution should likewise be diluted with a large quantity of water before decomposing it. When the nitric acid which is submitted to treatment with sulphuretted hydrogen is abundant, and not much diluted, its decomposition may produce some ammonia, a phenomenon to which Johnston was the first to call the attention of chemists.

When nitric acid is combined with a metallic oxyde capable of being completely precipitated from its solution by sulphuretted hydrogen in the state of metallic sulphuret, the combination being at the same time insoluble in water, which is the case with a great number of basic nitrates, the salt may be mixed with a large quantity of water, and a current of sulphuretted hydrogen is passed through the mixture until it ceases to be absorbed. The best is to make the mixture in a bottle capable of being closed with a glass stopper. When sulphuretted hydrogen has been passed for a long time through the mixture, and the latter smells strongly of sulphuretted hydrogen, even

after having removed the apparatus from which the gas was disengaged, the bottle is closed up, and it is agitated for some time in order to decompose the portions of the combination which might have escaped the action of the gas. If, on opening the bottle, the liquor has still a strong odour of sulphuretted hydrogen, the decomposition is complete. In the contrary case, sulphuretted hydrogen must be again passed through the liquor. The liquor filtered from the metallic sulphuret produced, and which contains nitric acid, is afterwards treated according to the method which I have prescribed for the decomposition of the nitrates which are soluble in water.

The nitrates which are insoluble in water may also be analysed in the following manner, which was first published by Mitscherlich, junior:—A certain quantity of the salt to be examined is weighed, a solution of sulphuret of barium is poured upon it, and the whole is left in digestion in a bottle which can be corked up. The metallic sulphuret produced is collected on a filter, and a current of carbonic acid is passed through the filtered liquor, which contains nitrate of baryta and the excess of sulphuret of barium employed. This current of carbonic acid converts the sulphuret of barium into carbonate of baryta, under disengagement of sulphuretted hydrogen. This decomposition, however, is very slow, and often requires that the current of carbonic acid should be continued for twenty-four hours. It is advisable to evaporate the whole to dryness, and to treat the dry residuum by water, which dissolves the nitrate of baryta only, the quantity of which is determined as was said above.

When either this or the preceding methods are employed, it is necessary to pulverise the nitrate insoluble in water, as finely as possible, before weighing it, because otherwise it might happen that portions of this salt would escape the action of the sulphuretted hydrogen or of the sulphuret of barium.

If the nitrate to be analysed contains a metallic oxyde which cannot be completely precipitated in the state of metallic sulphuret from a neutral solution by sulphuretted hydrogen, and can be so precipitated only by the soluble sulphurets of the alkaline metals or earths, which is the case with the oxydes of manganese, of iron, of zinc, and of cobalt, the solution of such a salt, or, if insoluble, a given weight of its powder, is treated by a solution of sulphuret of barium according to the method which has been described before.

When the compound to be analysed is soluble in water, and is a combination of nitric acid with a base which can be precipitated completely from its solution by hydrate of baryta, which is the case with most metallic oxydes, the process to be followed for finding the quantity of the nitric acid is much more simple. A certain quantity of the salt is weighed, and put in digestion with an excess of a solution of hydrate of baryta, and the mixture is boiled. The whole is then evaporated slowly and carefully to dryness, and the dry residuum is treated by water, which dissolves only the nitrate of baryta, leaving carbonate of baryta and the base which the baryta has precipitated.

When the solutions of nitrate of baryta and of strontia have to be analysed, they must be first decomposed by sulphuric acid, in order to calculate the quantity of the base from that of the sulphate of strontia or of baryta obtained. A solution of hydrate of baryta is then poured in the filtered liquor, in order to remove the excess of sulphuric acid employed, and the nitric acid is then determined by the process which has been mentioned several times.

\* The methods which have been described may be used to determine immediately in most nitrates not only the quantity of the base, but likewise that of the nitric acid. When these salts contain water of crystallisation, the loss indicates its amount.

It is only in some nitrates that the quantity of the nitric acid cannot be determined in an immediate manner, but must be calculated from the loss. This is the case, for example, with the combinations which nitric acid forms with the alkalies. Such salts must be decomposed by sulphuric acid, and from the quantity of sulphate of alkali obtained that of the alkali is determined, and the loss indicates that of the nitric acid.

When, however, a solution contains nitrates of alkalies, and the operator wishes to determine accurately the quantity of the nitric acid, the following method may be employed. Sulphuric acid is added to the solution, and the whole is distilled to dryness in a retort, at a moderate heat; the product is collected in a glass receiver, which contains a solution of hydrate of baryta. The operator must take care that no acid is lost by volatilisation. When the distillation is finished, the liquor in the receiver is evaporated to dryness, and water is poured upon the dry residuum, which dissolves the nitrate, and leaves the carbonate of baryta. The latter may be mixed with sulphate of baryta if, during the distillation, sulphuric acid has passed over in the receiver. The quantity of the nitric acid is determined by means of sulphuric acid, as was said above. This method may be very advantageously employed for the determination of the mineral or well waters which contain nitrates.

\* The analysis of the solid nitrates may be performed like that of nitrogenised organic substances, by means of protoxyde of copper, as will be shown farther on.<sup>1</sup>

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<sup>1</sup> Count Schaffgotsch proposed to determine the amount of nitric acid in anhydrous insoluble nitrates by fusion with borax, as follows :—The nitrate to be analysed is reduced to extremely fine powder by levigation, and mixed with about two or three parts of perfectly anhydrous borax, and being put in a platinum crucible, the whole is weighed and submitted to a gentle heat, gradually augmenting until the mass undergoes tranquil fusion. The whole is then allowed to cool and weighed again; the difference between the original weight indicates the quantity of the nitric acid contained in the nitrate operated upon.—Ep.

## DETERMINATION OF NITROUS ACID.

The best method of analysing the combinations of nitrous acid consists in determining the quantity of base which they contain, and estimating that of the acid from the loss. The nitrates may be decomposed by sulphuric acid, and their composition calculated from the weight of the sulphate obtained. The nitrous acid may also be destroyed by igniting the salt, and then determining the quantity of base which remains. It is difficult when these methods are resorted to, to ascertain how much water of crystallisation the combination contains.

\* The method of calculating the quantity of the nitrous acid from the loss, after having determined that of the nitrates, is not the only one which can be employed to ascertain the quantity of acid contained in the salts. This may be done by converting the nitrous into nitric acid, from the quantity of which that of the nitrous acid is calculated. The best manner of operating consists in mixing a certain weight of nitrate with hydrate of peroxyde of barium, and pouring water upon the mixture; the whole is then left in digestion, the nitrous acid becomes converted into nitric acid; the excess of peroxyde is decomposed by boiling, which thus produces hydrate of baryta under disengagement of oxygen. This being done, the quantity of the nitrate of baryta produced is determined as was said (page 613).

\* Instead of peroxyde of barium, red lead or peroxyde of lead might be used for the purpose of transforming nitrous into nitric acid. But as nitric acid forms with protoxyde of lead basic salts, which are insoluble, the nitrate of lead formed cannot be well separated from the excess of the peroxyde of lead employed.

\* The nitrites, like the nitrates of alkalies, may be analysed by means of protoxyde of copper.

All the degrees of oxydisation of nitrogen may be completely



decomposed by passing their vapour over red hot copper or iron. Dulong was the first who employed this method for the analysis of anhydrous nitrous acid. He made use of a porcelain tube, into which he introduced a known weight of copper or iron wire, well scoured and in great excess. The two extremities of the tube were furnished each with a cork traversed by a glass tube. One of these tubes served to lead the gas into the porcelain tube, the other served for its exit after decomposition, in order to measure its volume. The gas issuing from the porcelain tube, was passed also through a glass tube full of chloride of calcium, in order to deprive it of all moisture. The portion of the porcelain tube containing the metallic wire was heated to redness and the gas was then passed through it, the result was a production of peroxyde of iron or of copper and nitrogen gas. After the experiment, the metallic wire was weighed, in order to determine the weight of the oxyde, and the volume of the nitrogen gas collected was measured. When the combination contains water, a portion of it is absorbed by the chloride of calcium, and the other portion is decomposed when iron has been employed, in which case the nitrogen is mixed with hydrogen. The mixtures of nitrogen gas with other gases are analysed in another manner, but this subject will be treated of when we come to speak of the analysis of gases.

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Note by M. E. Peligot.

\* The quantitative determination of the nitrous acid of nitrites, from the loss which these salts sustain by ignition, may be a source of serious errors, especially on account of the difficulty of determining the water of crystallisation in an accurate manner; the operator never knows exactly how to portion the loss, and thus nothing is more easy than to mistake for water of crystallisation a part of the oxygen belonging to the acid.

\* This confusion may be avoided by the use of the following method, by which I have been enabled to distinguish in the products which resulted from the contact of nitrate of lead,

dissolved in water with lead, two kinds of crystallisable salts, the one formed by hyponitric acid  $\text{NO}_2$ , the others by nitrous acid  $\text{NO}$ .

\* When a salt formed by one or the other of the acids is put in contact with acetic acid, taking care to add it gradually in order to prevent the liquor from becoming warm, the salt dissolves without producing any gas. Thus, whilst the mineral acids disengage nitrous fumes from the combinations, acetic acid, even in the concentrated state, and, though used in large excess, dissolves them without alteration, provided all elevation of temperature is guarded against. If, then, a given weight of pure peroxyde of lead is put in contact with this solution, after stirring the mixture for some time, the nitrous or the hyponitric acid is converted into nitric acid; the result of this experiment is that a quantity of peroxyde of lead proportionate to the quantity of the oxygen absorbed is dissolved, so that the nitrous acid dissolves double the quantity of peroxyde of lead than hyponitric acid.

\* The soluble mixture of the nitrates and acetates formed is separated from the remaining peroxyde, the weight of which oxyde, previously well washed, and dried, being compared with its original weight, shows the quantity which has been dissolved by a given weight of the salt submitted to analyses.

\* It is essentially necessary that the peroxyde of lead employed should contain no protoxyde nor minium, in which state it can be obtained only by repeated washings with hot dilute nitric acid, until it ceases to dissolve anything. Moreover, this substance being very hygroscopic, it must be weighed in the same external conditions before and after its contact with the salts submitted to analyses, and with the acetic acid.

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#### SEPARATION OF NITROGEN FROM PHOSPHORUS.

The combination of nitrogen and phosphorus, which is non-volatile and infusible out of the contact of the air, and which

resists the most powerful reagents, may be quantitatively analysed as follows :—A weighed portion thereof is mixed with a weighed portion of recently ignited protoxyde of lead, and nitric acid is poured upon the mixture. The whole is then evaporated to dryness, the dry mass is carefully ignited until all the nitrate of lead produced is completely destroyed. The phosphate of lead remains, the quantity of which is determined from the excess of weight which the protoxyde of lead has acquired. From the quantity of the phosphoric acid, that of the phosphorus contained in the combination is calculated. That of the nitrogen is known from the loss ; any other mode of determining it is attended with the greatest difficulties, and does not yield accurate results.

#### SEPARATION OF NITROGEN FROM CHLORINE AND IODINE.

The ease with which the combination of nitrogen and of chlorine or iodine is decomposed, renders the rigorous analysis of these compounds difficult and even dangerous ; considering that these compounds are resolved into their elements when submitted to a high temperature, this process might be employed to determine the proportion of their constituents ; but it is impossible to collect completely the products of the combustion, because it is accompanied by a violent explosion. When such combinations are treated by copper and water, compounds of copper and of chlorine or of iodine are obtained, whilst nitrogen is liberated. The quantity of the chlorine or of the iodine may be accurately determined in the new compounds which have been thus produced ; the nitrogen which has disengaged is collected, and its volume is measured.

#### SEPARATION OF NITROGEN FROM CARBON—ANALYSIS OF THE COMBINATIONS OF CYANOGEN.

The combinations of carbon and of nitrogen (cyanogen) with other substances are very important. They may be analysed by determining accurately the quantity of the metal, and

calculating that of the cyanogen from the loss. Most of these combinations are converted into metallic chlorides, under disengagement of hydrocyanic acid gas, when treated by muriatic acid. The weight of the metallic chloride produced is determined, and thus the composition of the metallic cyanuret is easily found, provided the latter contains no water of crystallisation.

If the cyanogen is combined with such metals as can be precipitated completely from their solutions by sulphuretted hydrogen in the state of metallic sulphurets, this gas may be employed to effect the decomposition, even when the cyanuret is insoluble in water, in which case it suffices to mix the latter with water and to pass a current of sulphuretted hydrogen through the liquor. The metal is thus converted into metallic sulphuret, and its quantity may then be determined. The liquor filtered from the metallic sulphuret contains hydrocyanic acid.

\* Chemists have not, however, examined yet, whether all the metals which are capable of being converted into sulphurets by sulphuretted hydrogen lose this property when they are in the state of simple cyanides. The cyanides of mercury and of silver may be thus reduced, both of them; the first, when in the state of solution in water, and they are completely converted into sulphurets by sulphuretted hydrogen.

If the operator wishes to determine the quantity of the cyanogen immediately, he may do it in the following manner:— A certain portion of the cyanuret is weighed and mixed with a suitable quantity of protoxyde of copper, and the mixture is ignited. The cyanogen is converted into carbonic acid gas and into nitrogen gas, so that the gaseous mixture contains two volumes of the first and one volume of the second. The operator may afterwards, from the volume of this gaseous mixture, determine the quantity of the cyanogen which was contained in

the combination. It is necessary, however, that the cyanogen be not combined with the metal of an alkali or of an alkaline earth. All the precautions which it is necessary to take, in order to obtain an accurate result, will be described fully in the next chapter.

The double metallic cyanurets are much more frequently produced than the simple metallic cyanurets, and the combinations of that kind most frequently met with are those of iron with other cyanurets. That which renders the analysis of these cyanurets more difficult than that of the simple cyanurets is, that they are much more difficult to decompose in many cases; they are not acted upon by sulphuretted hydrogen even in presence of metals which, when contained in other combinations, are completely precipitated from their solutions by this reagent in the state of metallic sulphurets. According to Rammelsberg, the combinations of the cyanurets of cadmium, of mercury, and of silver, with other metallic cyanurets, particularly those of potassium and of sodium, are easily and completely precipitated from their solutions by sulphuretted hydrogen or hydrosulphuret of ammonia, in the state of metallic sulphurets, and therefore these reagents may very conveniently be employed to analyse them. On the contrary, the combinations of the cyanurets of iron, of nickel, of cobalt, of copper, of manganese, of zinc, with those of potassium and of sodium, are not precipitated from their solutions in the state of sulphurets by sulphuretted hydrogen or hydrosulphuret of ammonia, or at least are precipitated by these reagents only after a very long time, and in an incomplete manner.

\* Several other reagents, which precipitate completely from other liquors the metals of which I have been speaking, for example, the solutions of alkalies, do not precipitate these metals when combined with cyanogen, and form double cyanurets.

The best reagent for the analysis of the double cyanurets is

concentrated sulphuric acid, and yet heat must be applied, for at the ordinary or at a low temperature they often dissolve them only, without decomposing them. When the decomposition is effected with the application of heat, it must be increased in order to volatilise the excess of sulphuric acid. From the quantity of the sulphates obtained the composition of the cyanuret is ascertained.

In some cases, however, the decomposition of these double cyanurets may be effected as follows:—A given weight of the combination is to be pulverised, and put in a flask, fuming nitric acid is poured upon it, and the whole is heated for a long time after the first action of the acid is over, and muriatic acid is then added. The metals which are combined with the cyanogen are thus converted into oxydes. It is necessary to digest the combination for a very long time with fuming nitric acid, or aqua regia, in order that the decomposition may be complete. When fuming nitric acid is employed, the decomposition is ordinarily accompanied by a disengagement of hydrocyanic acid. From the quantity of the metallic oxydes obtained that of the metals is calculated, that of the cyanogen is afterwards estimated from the loss, if the combination contained no water of crystallisation. The use of concentrated sulphuric acid, however, is almost always preferable for the purpose to that of nitric acid, for the decomposition by the latter is always much more difficult and often incomplete.

The decomposition of the combinations of cyanogen may also be effected in many cases, by peroxyde of mercury. When the solution of a combination of that kind, or, if insoluble, a mixture of its powder with water, is boiled with an excess of peroxyde of mercury, the latter substance oxydises the metals combined with the cyanogen, whilst the reduced mercury unites with the latter, and produces cyanuret of mercury which dissolves. If the combination employed contains protocyanuret of iron, or percyanuret of iron, the iron is converted into peroxyde of iron,

which separates. A long digestion, however, is necessary to precipitate it completely. It is then collected on a filter and ignited; after ignition pure peroxyde of iron remains, the excess of peroxyde of mercury which was mixed with the latter having been volatilised. This method of analysis does not appear, however, to deserve being much recommended, because peroxyde of mercury does not effect a complete decomposition. When the combination of cyanogen contains cyanuret of potassium, potash, according to L. Gmelin, is precipitated along with the peroxyde of iron, which cannot be separated by washing.

The decomposition of the double cyanurets may also be effected by ignition in the air, but in that case, they must be kept for a long time exposed to a red heat, especially when they contain cyanuret of potassium, or of sodium. The metals of the combination are then obtained in the state of oxydes, which may afterwards be separated from each other.

\* The metals of some of the double cyanurets may be reduced by hydrogen gas, after having first destroyed the cyanogen by means of chlorine. Rammelsberg operating upon the double cyanurets of gold, of platinum, of palladium, and of iridium, at times evaporated their solution to dryness with aqua regia, at other times heated the dry salts in a current of chlorine gas; in either case, reduction was effected by hydrogen gas.

If the operator wishes to determine immediately the quantity of cyanogen contained in such combinations, he may treat them exactly as he would the simple metallic cyanuret. A certain weighed quantity is ignited with protoxyde of copper, and the quantity of the cyanogen contained in the combination, is determined from the gaseous mixture obtained, and which consists of one volume of nitrogen gas, and two volumes of carbonic acid gas. If, in this experiment, water is obtained, it existed in the state of water of crystallisation, or of hygroscopic water in the combination.

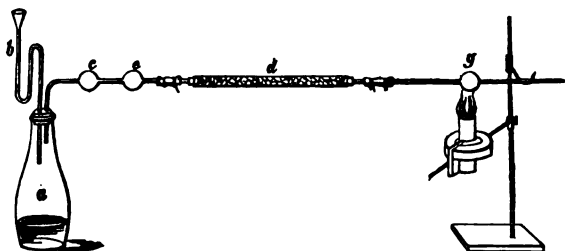
It is often very easy to determine the quantity of the water of crystallisation in these combinations by heating them gently, and determining that quantity of water from the loss of weight which they thus sustain. It is sufficient to keep the combinations of protocyanuret of iron with cyanuret of potassium, or of sodium, either in a warm place, or under the receiver of the air-pump by the side of a dish of sulphuric acid, to deprive them of all the water of crystallisation. On the contrary, the combinations of protocyanuret of iron with cyanuret of barium, or with cyanuret of calcium, obstinately retain a small portion of their water of crystallisation, which cannot be determined, except by decomposing these combinations by means of protoxyde of copper.

With respect to the combination of cyanogen with oxygen, and those which the different acids of that body produce by their union with the bases, the best method of analysing them as accurately as possible, consists likewise in determining the quantity of base which they contain. When the operator wishes to find immediately the quantity of cyanogen contained in the acids, a given weight of the salt, (the quantity of the base of which, and consequently, that of the acid, is known) is heated with the protoxyde of copper. In this experiment the operator should obtain a gaseous mixture containing two volumes of carbonic acid gas, and one volume of nitrogen gas; from the volume of this mixture, the quantity of the cyanogen is determined. In order to estimate the quantity of the base in cyanates, Wöhler recommends the following method in addition to those which are employed for the cyanurets. A current of dry muriatic acid gas is passed over a weighed quantity of the salt, heated by means of a spirit-lamp. The apparatus described, (page 138), and again reproduced here, may be used for the purpose.

A great quantity of carbonic acid, and of muriate of ammonia, are formed, which would obstruct the orifice of the tube, if it were too narrow. The muriate of ammonia is expelled



by heat, and when the apparatus has cooled, the metallic chloride produced is weighed, from which, the quantity of the base becomes known.



As cyanic acid is easily decomposed into ammonia and carbonic acid in those of its combinations which are soluble in water, owing to which the bases are converted into carbonates, Wöhler recommends to take advantage of this property to analyse them. The salt is moistened in a platinum crucible, gently dried, and ignited; this treatment is repeated several times, and at the end the operator obtains the base of the cyanate united with carbonic acid, unless the latter is dissipated by the red heat. During this treatment there is a disengagement of ammonia.

The cyanates dissolved in water, and those which are insoluble in this menstruum, may also be decomposed by muriatic acid. The whole is evaporated to dryness, and the residuum ignited, and from the quantity of the metallic chloride obtained, the composition of the salt is calculated. The bases which were combined with the cyanic acid might be separated from the salts dissolved in water, according to the methods which have been described before. With respect to the cyanates which are insoluble in water, it is sufficient to dissolve them in an acid, for the purpose of determining quantitatively the bases contained in the solution.

## CHAPTER LIII.

## HYDROGEN.

## DETERMINATION OF WATER.

\* THE combination of hydrogen and oxygen which form water, is a substance so very common that its quantitative determination is of the greatest importance. It may be attained in various ways, according to the nature of the bodies with which water is combined.

\* All substances reduced to powder absorb moisture from the air—wherefore the weighing of pulverulent precipitates, after they have been ignited, leaves a slight degree of uncertainty in certain substances, such as silicic acid, protoxyde of copper, &c., attracting moisture more easily or more rapidly than others. In order to weigh, after ignition, a substance which has been as much as possible deprived of this moisture, it is ignited in a covered platinum crucible, and the crucible is put in a small capsula, and surrounded by concentrated sulphuric acid, a glass bell is put over the whole, and it is left to cool. When completely cold it is weighed with all possible diligence.

\* The fused precipitates, for example, chloride of silver, do not attract moisture, and may remain exposed for a long time without increasing in weight.

\* The method which is most ordinarily employed to deter-

mine water in most inorganic substances of which it forms an essential constituent, consists in igniting a small quantity, previously weighed, of the inorganic substance in a platinum crucible, by which means the water is volatilised ; after cooling, the residuum is weighed, and the difference of the two weights indicates the quantity of water. This method may be employed when the substance to be ignited is not capable of undergoing, by this treatment, any other alteration than the loss of its water.

\* The quantity of the water of crystallisation of a very great number of salts is determined by this method. The platinum crucible in which the salt has been weighed is covered up and heated very slowly. The larger the quantity of the water of crystallisation contained in the salt, the more slowly must it be heated in order to avoid all chance of loss by projection. Yet, when the quantity of the water is so considerable that the salt fuses at a moderate heat, which is the case, for example, with several of the salts of soda, the salt must be heated very slowly, and for a long time, in a platinum crucible, so that it may not fuse; when it has thus lost the greatest portion of its water, the heat is gently increased, and ultimately it is ignited, after which the crucible is weighed.

\* If the salt is not decomposed by the heat of an argand spirit-lamp, it may be thus heated in a platinum crucible as strongly as possible, because there are certain salts, for example, the arseniate and phosphate of soda, which obstinately retain a small quantity of water. It often happens that when the ignition lasts too long, the salts undergo partial decomposition; such is the case, for example, with a great number of metallic sulphates. In that case, the heat must not exceed incipient redness.

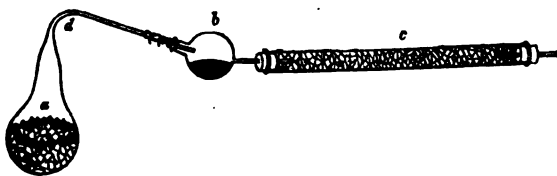
\* Several salts, however, being heated in a platinum crucible, even though it be closed, may, whilst they lose their water,

absorb oxygen or carbonic acid from the atmosphere, and thus pass to a higher degree of oxydisation, or in the state of carbonates. The first case occurs, for example, when the proto-salts of iron which contain water are thus treated; several basic salts illustrate the second case. If saline substances have to be deprived of their water, they are introduced into a small retort in order to shelter them from the air during the ignition.

\* The operator then proceeds in the following manner:— a bulb is blown at the end of a glass tube, so as to form a small bottle. The glass tube taken for the purpose should be strong, in order that the bulb may not be softened by the first impression of the heat. The little bottle is then weighed, and as much of the substance as he wishes to examine is introduced into it, and with the feather of a quill he cleanses the tube, or detaches the small particles which might adhere to it, and again weighs the bottle to know the weight of the substance experimented upon. This done, the tube of the small bottle is drawn out to a point at about one inch from the bulb, and it is bent so as to form a small retort; the weight is again taken. The body of this small retort is now heated to redness, and gradually augmented to the highest point which the glass can bear. The water in the neck of the retort is completely expelled by means of a small spirit-lamp. When aqueous vapours cease to condense in the neck of the retort, the extremity of the neck is sealed up by the flame of the spirit-lamp, whilst the body of the retort is kept red hot, taking care that no particle of the glass is chipped and lost. The whole is then allowed to cool completely; the point is carefully cut off with a file, and the retort is weighed with this point. The loss of weight indicates the quantity of water which was contained in the substance. As the combination has cooled out of the contact of the air, it cannot have absorbed either oxygen or carbonic acid; but the pointed extremity of the retort having been soldered up whilst the retort was still red hot, the air contained in it is very rarefied, so that if this extremity were not cut off

with a file, a greater loss of weight would be noted, and consequently, a greater quantity of water than was really contained in the compound would be computed. It is therefore necessary to allow the retort to become filled with air again, whilst the substance, being quite cold, can no longer alter it.

If the operator wishes to determine the quantity of the water by an immediate weighing, not only in the substances which have been just mentioned, but, in general, in all those from which this liquid may be expelled by heat, the retort may be put in communication with a tube filled with chloride of calcium, which absorbs the water. This is done more especially when the heat expels from the substance under examination other volatile bodies, such as carbonic acid, for example. The apparatus used for the purpose, and the process employed, have been minutely described, (page 538).



\* Several salts which contain water of crystallisation, and which consist of weak bases, often lose, when heated by a spirit-lamp, not only their water of crystallisation, but also a part, or even the whole, of their acid, as is the case, for example, with sulphate of alumina, persulphate of iron, &c. When the base and the acid have to be quantitatively determined in these salts, the quantity of the water of crystallisation is estimated from the loss. The water may, however, be determined alone, and in a very exact manner, by taking a weighed portion of the salt, reduced into powder, mixing it with from four to six times its weight of protoxyde of lead, recently ignited, and accurately weighed. The mixture is effected in a platinum crucible, it is then closed up with its cover and submitted to a gentle heat at

first, and then increasing it until the protoxyde of lead begins to fuse. The acid of the weaker base unites with the protoxyde of lead, and cannot volatilise; the loss of weight is therefore due to water alone.

Yet, for all that, the perfectly accurate determination of the water of crystallisation of salts, presents the greatest difficulties. Besides the water of crystallisation which the salt contains in the state of chemical combination, all the salts which have crystallised in aqueous solutions, contain, besides, a certain quantity of water, mechanically enclosed, and the proportion of which is larger or smaller, according to the larger or smaller volume of the crystals. This water is due to the mother water interposed within the pores of the crystals. Large crystals often contain several per cents., but those which are very small ordinarily contain not more than one half per cent. of it. Salts may be freed from the greatest part of that water by pulverising them, and leaving them exposed upon filtering paper, at a temperature of about  $30^{\circ}$  or  $40^{\circ}$  cent. Yet, if the salts are of an efflorescent nature, as is the case with several of the salts of soda, they must be examined immediately after pulverisation, in order that they may not lose also a certain portion of the water chemically combined with them. If the salt be a deliquescent one, it may be dried by spreading it between sheets of filtering paper, putting it under a press, and renewing the paper until it ceases to become moist, after which the salt is rapidly submitted to experiment.

A great many salts contain no water of crystallisation, but their crystals contain water mechanically enclosed, when they have been obtained from an aqueous solution. If they are not capable of being destroyed by ignition, they may be freed from that water by exposing them to a red heat. If, on the contrary, they are decomposable by ignition, as is the case, for example, with the anhydrous nitrates, they must be strongly heated only, in order to expel the interposed water, but ordinarily, when

these salts are exposed to heat, they decrepitate with much violence, especially if their crystals are large, so that a great portion may be lost unless they be heated in a well closed crucible. The decrepitation is much less violent, however, if the salt before being heated has been pulverised as finely as possible, and left for some time in a place moderately warm.

Some of the salts which contain water of crystallisation lose also, when heated, the water which may be mechanically interposed between their crystals, and they then decrepitate. The only salts subject to this, are those which contain but little water of crystallisation, as, for example, bisulphate of potash, or those in which this water is an essential constituent, so that they are decomposed when it is expelled by heat, as, for example, hypophosphate of lime.

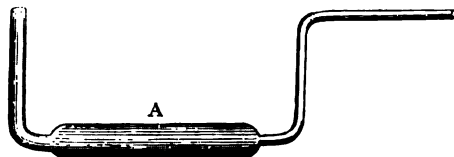
Many salts which contain water of crystallisation are decomposed the moment they begin to become red hot, so that the quantity of water which they contain cannot be deducted from the loss which they experience from the action of a strong heat. Yet some of these salts, for example, the nitrates, may be completely freed from their water when they are exposed at a temperature below a red heat, their acid not being decomposed at that temperature.

Other salts, on the contrary, especially those whose bases are combined with organic acids, cannot be thus heated, because they would be decomposed. Such salts should then be reduced into very fine powder, and placed under the receiver of an air-pump, near concentrated sulphuric acid; when they have remained for some time in vacuo under the receiver they are weighed, and from the diminution of weight the quantity of water which they have lost is determined. They are then replaced under the receiver of the air-pump, again left for some time in vacuo, near sulphuric acid, and weighed a second time. If the result of the first weighing is the same as the second, the operator concludes that the salt had already lost all its water at

the first weighing ; but if, on the contrary, the two weighings do not coincide, the salt must be placed a third time in *vacuo* with sulphuric acid, and the operation is repeated until the result of the two last weighings is identical ; the loss represents the water.

Some of these salts, however, retain their water of crystallisation, or at least part of it, with so much obstinacy that they cannot be freed from it, in which case the following method should be adopted in order to determine the quantity of this water of crystallisation. A certain portion of the salt is to be weighed, reduced into fine powder, and introduced into a vessel which is placed in a capsula full of hot sand. The temperature of the sand must not be such as to be capable of decomposing the salt. The capsula is then put near concentrated sulphuric acid, under the receiver of an air-pump, and a vacuum is rapidly made. After a certain time the salt is weighed, and replaced under the receiver. When some time has again elapsed, it is taken out and re-weighed, which operation must be repeated until the two last weighings agree with each other.

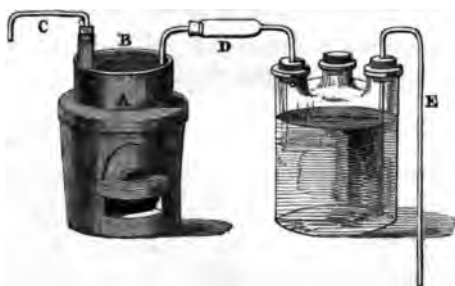
\* Often, in order to expel the water from certain substances, it is necessary to keep them exposed to heat for a long time, which heat, however, should not be too high, especially if the salt is an organic compound. When these substances have a great tendency to absorb water again during the weighings, it is best to employ the following apparatus, which was indicated by Liebig. The tube A, is employed to receive the



substance, which must be previously reduced into powder ; it (the tube) is first weighed when empty, and then again, after



the substance to be analysed has been introduced into it. It is connected by means of two corks, on one side with a glass tube C, on the other with a tube D, full of chloride of calcium, which communicates with a large flask full of water, the liquid of which may be removed by means of a syphon, E. The tube A is introduced into the iron pan B, containing either water or a concentrated solution of chloride of calcium, the temperature of which may be raised from  $50^{\circ}$  to  $125^{\circ}$  cent., or else with sand, by means of which a much higher temperature may be obtained. On removing the water from the bottle by the syphon E, a current of air is determined through the apparatus. This current



of air, together with the elevated temperature, rapidly expels the water from the substance, especially if another chloride of calcium tube is adapted to the tube C. Instead of the bottle full of water a small air-pump may be employed.

Instead of a glass bottle, any capacious air-tight vessel may be used, which must be connected with the tube, as represented in the figure, and from which the water may be let off by a cock, so that the rapidity of the flow of the water may be regulated.

\* The determination of the water of crystallisation of salts, of which it forms an essential constituent, and which are decomposed when heated before parting with this water, is attended with many difficulties. In such a case the quantity of the water is ordinarily determined from the products of the decomposition. Yet, no general rule can be prescribed in this respect,

because the methods which must be adopted vary with the constituents of the salt. All the phosphites and hypophosphites, for example, belong to this class.

I have already said (page 450) how the water which these salts contain can be determined.

\* In many other salts which contain water, as an essential constituent, the quantity of the water may be estimated by taking a given weight of the salt, igniting it as will be indicated farther on, with an excess of protoxyde of copper (*oxyde cuivrique*). If, besides water, the combination contains hydrogen also, this latter substance will have been completely converted into water, so that the water thus produced must be deducted from the total weight obtained.

It is not salts only which contain water, most acids contain it also; but generally it is so intimately combined with the latter, that it cannot be separated from them by a heat which otherwise would cause it to be volatilised. In such aqueous acids the water acts as a base, and in most cases it contains the same quantity of oxygen as the base with which the acid forms a neutral salt. Wherefore, in order to determine its quantity, the operator may take a given weight of the aqueous acid, and saturate it by a base capable of forming an anhydrous salt with the acid; the base unites then with it, and separates the water. The weight of the anhydrous salt is then determined, and if the quantity of the base employed is known, that of the water contained in the acid may be at once estimated by deducting the weight of the salt from the collective weight of the base and of the aqueous acid.

Recently ignited protoxyde of lead is the base which is generally employed in preference in this process. It is better suited than the earths and the alkalies to the purpose, because it does not absorb carbonic acid rapidly from the air. A certain quantity of the aqueous acid is weighed, it is dissolved in water,

and an excess of protoxyde of lead is added to it. The whole is then evaporated to dryness, and the residuum is ignited, if this may be done without decomposing the acid of the salt of lead. If, on the contrary, the acid is decomposable by ignition, the residuum must be left for a long time in a warm place, in order that all the water may evaporate. The loss of weight of the calcined or dried mixture of the salt of lead and of the excess of protoxyde of lead employed indicates the water which was combined with the acid.

If the aqueous acid forms with a base, a neutral and anhydrous compound which is perfectly insoluble, it is sufficient to mix together the aqueous solution of a known weight of the aqueous acid, and that of a salt of that base, in order to find, from the quantity of the neutral insoluble salt obtained, that of the water which existed in the acid. The various combinations of sulphuric acid with water are, however, the only ones in which the quantity of the latter may be thus determined. A given weight of the aqueous acid is to be dissolved in a large quantity of water, and a solution of chloride of barium is added to the liquor. From the quantity of sulphate of baryta obtained, that of the sulphuric acid is calculated, and it is then easy to estimate the quantity of the water with which the acid was combined before.

Other acids, for example, phosphoric acid, arsenic acid, &c., form, in combining with bases, salts which are insoluble in water, and yet the above process cannot be employed to find the quantity of water which they contain, because they form, with a same base, several salts which are insoluble in water, the neutral salt being precipitated, not in a pure state, but very often mixed with basic salts, even when the dissolved acid has been exactly neutralised by ammonia. A special analysis should then be made for determining the quantity of base existing in the precipitate which has formed. But such an analysis is more difficult still, and the result obtained

is always very inaccurate, because it very often happens that the combination produced is not absolutely insoluble in water. The best is, therefore, to determine the quantity of water in these acids by means of protoxyde of lead, according to the method described before, and which was indicated also (pages 331, 543).

When the operator wishes to determine the quantity of water contained in an aqueous acid in the solid state, it is sufficient to take a given weight of it and to mix it with a known weight of protoxyde of lead, recently ignited, and to expose the whole to a red heat, provided the combination thus produced is not capable of being decomposed by that temperature. The quantity of the water is then estimated from the loss of weight. If the acid forms with the protoxyde of lead, a very fusible combination, which is very often the case, the protoxyde of lead is put over the acid in a platinum crucible, and the whole is then heated with care. When the salt of protoxyde of lead which results from the reaction undergoes a slight decomposition by ignition in the air, the experiment must be performed in a retort, taking care not to heat it too strongly, for fear of the protoxyde of lead attacking the glass.

Several bases contain also water in the state of chemical combination, to separate it from some of which a strong heat is required, whilst a few others resist the strongest heat, and do not part with their water, such as, for example, potash and soda. The quantity of water contained in the latter substances is ascertained by dissolving a known weight of the base in a little water, and then supersaturating the solution by means of an acid capable of forming a neutral salt with that base, which cannot be decomposed by ignition, and from which the excess of acid employed may be easily expelled. Sulphuric acid may be employed for the purpose, or better still, muriatic acid, because it is much more difficult to expel the excess of sulphuric acid completely from sulphate of potash or of soda, than that of

muriatic acid from chloride of potassium or of sodium. From the quantity of neutral anhydrous sulphate, or chloride of alkali, the quantity of the dry alkali is calculated, which gives the quantity of the water with which it was combined before.

It is scarcely possible to indicate other general methods of determining the quantity of water contained in combinations. I have explained in the preceding paragraphs the particular processes which should be employed to determine quantitatively this water in compound substances which cannot be analysed in this respect by the ordinary method, that is to say, by heating the substance.

\* Some peculiar precautions must be taken for the determination or elimination of water contained in organic substances; I shall explain them farther on.

#### ANALYSIS OF MINERAL WATERS.

\* The quantitative analysis of mineral waters from their frequent employ in medicine is extremely important. I have given in the first part of this work the names of those substances which have been hitherto found in them, and which should be more particularly attended to. The course of the analysis of the various mineral waters is very often identical when they do not contain other constituents than usual.

\* The analysis of the water of salt-springs, of wells, of ordinary springs and of sea-water is performed nearly in the same manner as for several mineral waters.

\* The mineral waters which are intended for analysis ordinarily contain a great number of volatile substances, which, when they are left for a long time exposed to the air, are dissipated some time without having been decomposed by the air, such as carbonic acid gas; at other times after decomposition, as, for example, sulphuretted hydrogen gas. Certain mineral waters

contain such an abundance of carbonic acid, that when preserved in well corked bottles, a portion of the liquid is projected and is lost, on removing the cork. In order to determine the quantity of the gaseous substances contained in these waters a particular method is employed, which will be explained farther on.

\* In a great number of mineral waters the gaseous substance which they contain in a free state, are in extremely small quantity, and sometimes as inconsiderable as that of the ordinary atmospheric air which they absorb when left exposed for a long time. When such waters are quantitatively analysed, these gases are ordinarily neglected. To this class well-water, sea water, and that of salt-springs belong, all of which have remained for a long time in contact with the air. In such waters the operator determines only the quantity of the fixed constituents which is done in the same manner as for analysing the mineral waters which contain several gaseous substances in the free state

**ANALYSIS OF THE MINERAL WATER (CALLED ALKALINE) WHICH BESIDES FREE CARBONIC ACID, CONTAINS A LARGE PROPORTION OF CARBONATES OF ALKALIES AND OF EARTHS IN SOLUTION.**

**DETERMINATION OF THE FIXED CONSTITUENTS OF THE MINERAL WATER.**

\* In order to be able to measure exactly, without much trouble, the quantity of the mineral water experimented upon, a flask, provided with a glass stopper, of a well-known capacity, and which is known to contain so much distilled water at a certain temperature is employed, the stopper being so placed that the bottle is entirely full, and without a single air-bubble. This flask is then filled with the mineral water under examination, and it is weighed, in order to ascertain the specific gravity of the water. The same flask must be used during all the course of the analysis, not only to detect the quantities of the fixed constituents contained in the volume of mineral water operated

upon, but also if the operator possesses a sufficient quantity of the water, to determine separately one or the other of the constituents in a known quantity of that water.

\* If the mineral water contains much carbonic acid ; before taking the specific gravity, it must be left in an open vessel until bubbles cease to be deposited on the inside of the vessel. Sometimes a precipitate is produced at the same time ; this precipitate consists generally of peroxyde of iron which was kept in solution in the water by free carbonic acid. This precaution is necessary, and must be observed for all the quantities of the mineral water which the operator intends to devote to the research of the fixed constituents.

\* A. The contents of one or of several flasks is carefully evaporated to dryness. This had better be done in a counterpoised platinum capsula, but if such a capsula is not at hand, one of porcelain or of glass may be employed. The evaporation must take place at a very gentle heat, without ever allowing the water to boil. The operator likewise must take care, as indeed in all such evaporations, to cover the capsula with filtering paper, in order that no dust may fall in the water. After evaporating to dryness, the heat is increased under the capsula to incipient redness. It is then weighed again, and the quantity of the fixed constituents contained therein becomes thus known.

\* Most mineral waters contain larger or smaller quantities of organic matter in solution, owing to which the fixed constituents of such waters become brownish or black when strongly ignited. It is not possible to determine with accuracy the quantity of organic matter contained in the mineral water, for if evaporated only to such a point that the organic matter is not destroyed, its hygroscopic property renders it difficult to determine the quantity of the fixed constituents. It is better, therefore, to ignite the fixed residuum in the air until the organic matter is almost entirely destroyed, provided it is

not too abundant, or its exact nature is not a matter of particular inquiry. When this organic matter is contained in too large quantities in the mineral water, it is often difficult to destroy it by heat, and it often happens that in burning it some of the inorganic constituents of the water are decomposed also.<sup>1</sup>

\* When the mineral water contains only very few fixed substances, and the operator is consequently obliged to evaporate a great quantity of it in a capsula too large to be counterpoised, he is often under the necessity to forego the quantitative determination of these fixed constituents, because it is very difficult to transvase them from a large capsula into a small one, because some of these constituents stick with great force during the evaporation to the sides of the vessel, from which they cannot be detached.

In such a case it is not necessary to evaporate the mineral water to dryness, but only until the soluble salts crystallise.

\* B. The fixed substances which have been weighed, or the mass which has not been completely dried, must now be treated by water. The substances which are insoluble in water are collected and washed upon a weighed filter as small as possible; they are then dried as much as practicable and weighed. They consist principally of silicic acid, of earthy carbonate, and of carbonate of peroxyde of iron, which ordinarily existed in solution in the water in the state of bicarbonates; sometimes, also, they contain phosphoric acid and even combinations of fluorine. If the fixed constituents have been heated too strongly after the evaporation of the water, the carbonate of magnesia, if present, may have lost its carbonic acid.

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<sup>1</sup> In order to determine the amount of organic matter, a known portion of the water containing it should be mixed with carbonate of soda and evaporated to dryness; the residuum should then be treated by boiling water, filtered, and evaporated to dryness, at a temperature not above 140° cent. (284° Fahr.), until the weight remains constant. This dry residuum is then exposed at a low red heat, until the black colour of the mass is destroyed. The difference of weight before and after the ignition indicates the quantity of the organic matter.—Ed.



The silicic acid which exists in mineral waters is probably, in most cases, one of the constituents of the organic substances. It is very probable that it is owing to the presence of certain animalcula with silicious coat (*Bacillariæ* and *Naviculæ*).

\* It is possible that this may be also the case with the peroxyde of iron of mineral waters, when this oxyde does not exist in solution therein, but forms an ochreous deposit. This deposit consists often of animalcula or infusoria with coating of peroxyde of iron with a little silicic acid. (*Gallionella ferruginea* et *aurichalcea* of Ehrenberg.)

\* C. If the analysis is required to be strictly accurate, the solution of the salts soluble in water may be evaporated again to dryness, and the residuum ignited. The object of this experiment is to determine their weight in an immediate manner, and not from the loss which is indicated after having weighed the insoluble salt. When the weight of the latter has been determined with sufficient accuracy, this evaporation may be dispensed with.

\* When, however, the solution has been evaporated, the salts, after being weighed, are dissolved in water; it sometimes happens that the latter leaves a very small residuum, which ordinarily is magnesia, the weight of which must be determined.

\* The liquor is afterwards carefully supersaturated with acetic acid, and then again evaporated to dryness. If the alkaline salt had dissolved a little silicic acid, the latter remains behind; in the contrary case the solution is clear.

\* The evaporation may be dispensed with when the quantity of silicic acid in the water is very slight.

\* If, however, the liquor have been evaporated, it is to be filtered from the silicic acid, and it is then found to contain no other acid than sulphuric and muriatic acids. The saturation by acetic acid expelled the carbonic acid which was contained in the soluble salts.

\* A solution of acetate or of nitrate of baryta is poured in

the liquor, to which acetic or nitric acid has previously been added. The sulphate of baryta obtained is ignited and weighed and from its quantity, that of the sulphuric acid which exists in the mineral water is calculated. When carbonate of alkali was amongst the soluble salts, the mineral water contains nothing else than the above acids.

\* To the liquor which has been separated from the sulphate of baryta produced, a solution of nitrate of silver is added in order to precipitate the muriatic acid in the state of chloride of silver, the quantity of which is accurately determined. The salt contains, then, all the chlorine which existed in the mineral water.

\* If the mineral water contains a combination of iodine iodide of silver is precipitated with the chloride of this metal. Ammonia may be employed in the analysis of mineral water to separate it from the latter.

\* If a combination of bromine be present, bromide of silver is precipitated also.

\* I have shown (pages 603, 609) how bromine can be separated from iodine when the quantity of the mineral water is in sufficient abundance.

\* As it is of the highest importance, in these analyses, to determine with great accuracy the proportion of the sulphuric and of the muriatic acids, it is advisable, if a great quantity of mineral water can be had, to operate upon fresh portions of the water, in order to determine these two acids. A portion thereof equal in bulk to the capacity of the flask spoken of above is devoted to the determination of the sulphuric acid. Muriatic acid is then added to the water, and a solution of chloride of barium is poured in, which precipitates the sulphuric acid in the state of sulphate of baryta. It is not necessary to determine the sulphuric acid separately, when the mineral water contains a little phosphate of alkali amongst its soluble salts.

for, as will be seen farther on, the determination of the sulphuric acid may be effected in an accurate manner simultaneously with that of the phosphoric acid.

\* Another volume of mineral water, equal to the capacity of the bottle, is acidified with nitric acid, and a solution of nitrate of silver is poured into it, in order to ascertain the quantity of the muriatic acid.

\* D. The base of the acids in the soluble salts is ordinarily soda. The mineral water, however, may contain potash, or even lithia. Very small quantities of phosphoric acid may even be combined with these alkalies, though, if lithia, and especially lime, be present, they may be almost imponderable.

\* Another volume of the mineral water is treated as above, (see B.), in order to obtain a fresh quantity of the fixed constituents, which must be submitted to the same process as before, in order to separate the soluble from the insoluble salts. The solution of the soluble salts is supersaturated by means of muriatic acid, and chloride of barium is poured in for the purpose of separating the sulphuric acid. The sulphate of baryta thus obtained, may be determined from its weight, which should be compared with that of the former analysis, the result of which it should thus confirm. The liquor filtered therefrom is evaporated, in order to reduce it to a smaller bulk, and it is then poured in a flask capable of being closed, and in which it is slightly supersaturated with ammonia. If a small quantity of phosphoric acid is present, it will be precipitated after some time, in the state of phosphate of baryta, the liquor being, of course, sheltered from the contact of the air. This salt is collected on a filter, as much out of the contact of the air as possible, and if in sufficient quantity it is weighed. When even its quantity admits of weighing, it is always too small to allow of the phosphoric acid being determined in the manner which has been indicated (page 439). It may be considered as an intermediary basic phosphate of baryta (phosphate

containing four-fifths of phosphoric acid) and the phosphoric acid which it contains is calculated from these *data*.

\* The liquor filtered from the phosphate of baryta, (if any was present,) is mixed with an excess of a solution of carbonate of ammonia, in order to eliminate the baryta, and after having collected the carbonate of baryta upon a filter, the liquor is evaporated to dryness. The dry residuum is ignited to expel the muriate of ammonia, and it consists of chloride of sodium; but it may contain also chloride of potassium, or even chloride of lithium. The ignited salt is dissolved in water, and a solution of chloride of platinum, or of soda-chloride of platinum is added, the whole is evaporated to dryness at a very gentle heat, and the residuum is dissolved in alcohol of specific gravity, 0.84. If the mineral water contained potash, there remains an insoluble potash-chloride of platinum, from the quantity of which, that of the chloride of potassium is determined, which must be deducted from that of the chloride of sodium, the exact quantity of which is now accurately known, provided, of course, that no chloride of lithium is present.

E. If the presence of lithia is suspected in the mineral water, or, if the qualitative analysis has already shown that it exists therein, and as its quantity is always inconsiderable, the whole of the soluble salts obtained from the dry residuum of a large volume of water of a known weight, must be devoted to its determination. To the solution of these salts, a solution of phosphate of soda, with a little carbonate of soda, is added, the whole is evaporated to dryness, and the double phosphate of soda, and of lithia, is obtained in the manner which has been indicated before (page 13). The operator calculates the quantity of chloride of lithium to which it corresponds, and it is deducted from the chloride of sodium obtained.

\* When the quantity of soda and the small quantities of potash and of lithia have been determined,—when, on the other hand, the operator has ascertained how much sulphuric and muriatic

acids the mineral water contains, the quantity of the sulphate of soda and of the chloride of sodium are calculated, and from the loss, that of the carbonic acid and of the carbonate of soda. The small quantity of potash may be calculated as sulphate of potash, and that of lithia as carbonate of lithia; but this method of proceeding is somewhat empirical, for it is admitting that in the saline mixture the strongest bases are combined with the strongest acids.

\* The carbonate of soda contained in the mineral water can be determined in another manner. According to Liebig, a known weight of the mineral water is taken, and its insoluble constituents (A., B.) are separated, muriate of ammonia is added to the solution, the latter is carefully evaporated to dryness, and the residuum is ignited, until all the ammoniacal salts are dissipated. Under the influence of heat, the muriate of ammonia decomposes the alkaline carbonates, and there remains a quantity of metallic chloride, corresponding to that of the carbonates. The residuum is dissolved in water, and the solution is again precipitated by solution of nitrate of silver (the solution having been first acidified with a few drops of nitric acid), which yields more chloride of silver than in the determination of chlorine mentioned at C. This latter quantity is deducted from the former, and from the excess of chloride of silver, the quantity of the carbonate of soda is calculated by means of the tables.

\* F. We have now to describe the process to be followed for analysing the constituents of the mineral waters which were insoluble in the water, by which the residuum of the evaporation was treated. They must be dissolved in nitric acid, and their solution is evaporated to dryness. The operation should be performed in a platinum crucible, covered during the evaporation with a plate of glass. If a combination of fluorine is present, the glass will be found slightly attacked, especially by breathing upon it. This is more readily produced by evaporating the

drops which have deposited on the glass. When the glass is not thus attacked, the operator may rest assured that no combination of fluorine is present.

\* The dry saline mass is moistened with nitric acid, and half an hour afterwards, water is poured upon it, which leaves the silicic acid in an insoluble state, and the weight of which is determined.

\* G. The nitric acid solution, filtered from the silicic acid, is then supersaturated with pure ammonia. The more or less considerable precipitate which is thus produced is filtered rapidly, and as much as possible, out of the contact of the air.

\* H. Taking now the liquor which has been separated from this precipitate, the lime contained therein is precipitated by oxalate of ammonia; but it may sometimes contain a trace of oxyde of manganese, when it exists in sufficient quantity in the mineral water (page 78). The oxalate of lime produced is converted into carbonate of lime in the manner which has been indicated (page 23). The quantity of oxyde of manganese is ordinarily so inconsiderable in the precipitate of oxalate of lime, that after having dissolved the carbonate of lime in muriatic acid, it can hardly be separated from the lime by hydrosulphuret of ammonia.

\* The precipitated lime may often contain strontia. After having weighed the carbonate of lime, it is dissolved in nitric acid, and the strontia which it contains ordinarily in very small quantity, is separated in the manner indicated (page 26). It is necessary to examine the strontia, and test it, to see whether it contains lime.

\* I. The liquor filtered from the oxalate of lime contains the greatest part of the magnesia existing in the mineral water. As no other acid, except nitric acid is present, it may be evaporated to dryness, and the dry residuum ignited, in order to obtain the magnesia. This method may be adopted, even when,

instead of nitric acid, muriatic of ammonia has been employed to dissolve the residuum, provided the precautions mentioned (page 46) be attended to. The calcined magnesia is weighed. Ordinarily, it still contains a little carbonate of soda, the latter forming with carbonate of magnesia, a very sparingly soluble double salt, which is decomposed by ignition, when the magnesia loses its carbonic acid. For the same reason, a little magnesia is diluted also in redissolving the salts soluble in water, as was said above at C.

\* The ignited residuum is treated by water, which dissolves the carbonate of soda, the solution of which is evaporated to dryness, in order to determine the quantity of this salt. It must be saturated with muriatic acid, in order to see whether a small quantity of a deliquescent salt will be produced, which would indicate the presence of magnesia in the carbonate of soda.

\* The calcined magnesia may still contain a little oxyde of manganese. It is dissolved, therefore, by muriatic acid, which often leaves a trace of silicic acid, the solution is then saturated by ammonia, and the operator endeavours to precipitate this oxyde in the state of sulphuret of manganese (*sulphure manganoux*) by means of hydrosulphuret of ammonia. It is sufficient afterwards to calcine the small quantity of the sulphuret obtained, and to calculate the residuum as manganoso-manganic oxyde. It is only after having deducted its weight from that of the carbonate of soda, that the quantity of the magnesia becomes known.

\* In order to be thoroughly convinced that the quantity of magnesia obtained is exact, the liquor filtered from the sulphuret of manganese is treated by muriatic acid, in order to destroy the excess of hydrosulphuret of ammonia, the magnesia in solution may be precipitated therefrom by means of phosphate of soda with addition of a little ammonia.

K. The precipitate which was produced by ammonia (at G.) in the nitric acid solution of the earths, is dissolved in muriatic

acid. This solution contains, in the state of peroxyde of iron, the whole of the protoxyde of this metal existing in the mineral water. Often also it contains small quantities of alumina and of phosphoric acid, and even, when the latter is somewhat abundant, lime and a little magnesia, the proportion of which is so much the more considerable, as the liquor filtered from the silicic acid was less acid.

\* The muriatic acid solution is supersaturated with a solution of pure potash with which it is subsequently boiled. The precipitate of peroxyde of iron thus obtained is dissolved in muriatic acid, and after saturating the solution by ammonia it is precipitated by hydrosulphuret of ammonia. The sulphuret of iron resulting therefrom, and which may contain a little sulphuret of manganese (*sulphure manganeux*) is strongly ignited in contact with the air, and thus converted into peroxyde of iron. If, however, the quantity of sulphuret of iron obtained is somewhat considerable, it is converted into peroxyde of iron in the manner described (page 86). The small quantity of manganese may be separated from the iron in the usual manner.

\* The liquor filtered from the sulphuret of iron, and which may contain a little phosphoric acid, with traces of other substances, is slightly supersaturated with muriatic acid, in order to destroy the hydrosulphuret of ammonia, and afterwards filtered to separate the sulphur. Ammonia being poured in the filtered muriatic acid, sulphur may produce a very slight precipitate, which consists principally of phosphates of magnesia and of lime.

\* The alkaline liquor filtered from the peroxyde of iron is supersaturated with muriatic acid. It is then left at rest for some time, and heated, in order that all the carbonic acid may be disengaged. Ammonia may then produce a slight precipitate, which may contain alumina and phosphoric acid. This precipitate is ordinarily so small that it is very difficult to separate its constituents by the method which was explained (page 437).



Wherefore the operator must rest satisfied in most cases with detecting the presence of phosphoric acid by means of boracic acid and iron-wire before the blowpipe, and with ascertaining that it contains no other base than alumina, which is already known to be the case, because the precipitate assumes a fine blue colour, when, after having moistened it with a solution of nitrate of cobalt, it is strongly heated before the blowpipe.

\* In the analysis of the precipitate obtained (at G.) by means of ammonia, the method which has been spoken of (page 443) may be advantageously employed. The precipitate is dissolved in muriatic acid, the solution is saturated with carbonate of ammonia, and the peroxyde of iron is precipitated by boiling.

\* If the mineral water contains a combination of fluorine, that combination is ordinarily found in the precipitate produced (in G.) by ammonia, because in general the fluorine exists in the state of fluoride of calcium. When in the course of the qualitative analysis, the operator has ascertained that the mineral water contains fluorine, the constituents of the water which, after evaporation, were left in an insoluble state, are to be dissolved in nitric acid, as was said (at F.), but the liquor must not be evaporated to dryness, in order to obtain the silicic acid. The liquor is filtered from the silicic acid, which has not been dissolved by the nitric acid, and it is afterwards supersaturated with ammonia; the precipitate is ignited and weighed, and after having put it in a platinum crucible, sulphuric acid is poured upon it, which disengages hydrofluoric acid, and even hydrofluosilicic acid, if the precipitate contained silica. The acid mass is then dissolved in a large quantity of water, and ammonia is poured in the solution, in order to precipitate the peroxyde of iron and likewise the phosphoric acid, alumina, and a trace of magnesia. The precipitate is filtered out of the contact of the air, and analysed, as was said before. Oxalate of ammonia is poured in the filtered liquor in order to precipitate the lime, which was contained in the mineral water in the state of fluoride of calcium.

\* If the mineral water to be analysed was forwarded in bottles or in jars closed with a cork, a part of the peroxyde of iron will have combined with the tannin of the cork, which is then coloured black; another more considerable portion will have deposited on the sides of the vessel, and adheres thereto with so much force that no mechanical power can detach it. The only resource in that case is to dissolve it by dilute muriatic acid; the blackened cork must likewise be digested in a little of this acid. The two muriatic acid solutions may then be mixed with the muriatic acid solution of the precipitate produced by ammonia (at G.)

\* In calculating the constituents of the mineral water which are insoluble in water, the quantity of fluorine formed is assumed to be fluoride of calcium, because it is probably in this state that it generally exists in the mineral waters. The lime, strontia, and magnesia are reckoned as simple carbonates, because it is in this state that they are found in the residuum insoluble in water, though they are contained in the state of bicarbonate in the mineral water. For the same reason the iron and manganese are assumed to be in the state of peroxyde of iron (sesquioxyde) and of sesquioxyde of manganese (*oxyde manganique*) though these metals are in the state of bicarbonates of iron and of manganese in the mineral water. The alumina exists in the state of phosphate, of sulphate, of alumina, or of chloride of aluminum.

\* The alkaline mineral waters generally form, at the place where the spring comes in contact with the atmosphere, deposits, the composition of which resembles that of the insoluble residuum obtained by evaporating water to dryness. These deposits may often be procured in very large quantity. As some constituents, for example, phosphoric acid, fluorine, alumina, strontia, protoxyde of manganese, &c., are sometimes contained in such minute quantities in the mineral water that their presence may be overlooked during the analysis, or it may be

impossible to determine their quantity, their deposits, therefore, have this advantage, that the above constituents may be quantitatively determined in them with much accuracy. It is necessary to make sure that the deposit has a composition perfectly identical with the insoluble residuum of the mineral water, and by analysing this deposit, all the constituents, even the rarest, may be calculated. Berzelius was the first to use this method for the analysis of the waters of Carlsbad<sup>1</sup>, and the examination of the deposit left by that water enabled him to detect some constituents which had been overlooked in former analyses.

\* The course of the analysis of a mineral water must be modified in an essential manner, when the quantity to be operated upon is small. In this case it is almost always impossible to determine the rare constituents, especially when the quantity of solid substances therein is small. If the operator has only a few ounces of liquid, the evaporation, with a view to determine the solid constituents, is of no avail, and therefore he must rest satisfied with deducing the quantity of the substances found from that of the liquid operated upon.

\* By the following process the constituents may be determined in a same small quantity of mineral water :—Nitric acid is to be added to a certain portion of the water, and by means of nitrate of silver, the quantity of chlorine is determined in the state of chloride of silver, and then, by means of a solution of nitrate of baryta, the quantity of sulphuric acid is determined in the state of sulphate of baryta. Sulphuretted hydrogen is passed through the filtered liquor, in order to separate the excess of oxyde of silver, and then, without filtering, sulphuric

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<sup>1</sup> The waters of Carlsbad have a temperature of about 164° to 167° Fahrenheit, and contain, according to Berzelius's elaborate analysis, 11·85 of carbonic acid, and 49·60719 of solid salts, consisting of carbonate of peroxyde of iron, carbonate of manganese, carbonate of soda, carbonate of lime, carbonate of strontia, carbonate of magnesia, chloride of sodium, sulphate of soda, silica, fluor spar, and subphosphate of alumina.

acid is added to remove the excess of baryta, after which, both the sulphuret of silver and the sulphate of baryta are simultaneously collected upon a filter. The precipitate must be well washed, in order to remove all the sulphate of lime which it might contain. The filtered liquor is saturated with ammonia, and oxalate of ammonia is added, in order to separate the lime in the state of oxalate of lime. The liquor filtered from the precipitate is evaporated to dryness, the dry residuum is ignited and weighed. During the ignition the residuum is treated by a little carbonate of ammonia. It is then dissolved in water, and the sulphuric acid is precipitated from the solution by acetate of baryta. The filtered liquor is evaporated to dryness, the residuum is ignited and treated by water, which dissolves the carbonate of soda, which should be examined, in order to see whether it contains potash. That which was not dissolved by water is redissolved in muriatic acid, and in treating the solution by dilute sulphuric acid, sulphate of magnesia is obtained, from which the quantity of magnesia is calculated. The weight of the magnesia and soda calculated as sulphates, must agree with the ignited mass from which the two substances have been extracted. From the sulphuric acid and chlorine found, the quantity of the sulphate of alkali and of the chloride of sodium are calculated. If there is more acid and chlorine than is adequate to the saturation of the alkali found, a portion of the sulphuric acid is contained in the mineral water combined with magnesia, and the other earths are in the state of bicarbonate.

DETERMINATION OF THE VOLATILE CONSTITUENTS OF THE  
MINERAL WATER.

\* Carbonic acid is ordinarily the only gas the volume of which has to be determined in mineral waters. This gas may be mixed with inconsiderable quantities of oxygen and of nitrogen. We shall speak farther on of the methods of determining sulphuretted hydrogen gas in mineral waters.

\* It is often very difficult to determine accurately the volume of carbonic acid gas dissolved in a mineral water. The mineral waters which contain a very large proportion of this gas, contain carbonate of alkalies and of earths in solution, in the state of bicarbonates, and it often contains besides as much free carbonic acid as the saline water can hold in solution at the temperature which characterises it. Ordinarily, the volume of the carbonic acid in solution is determined by boiling a given quantity of the mineral water, in order to expel all the gaseous constituents. Although the carbonic acid which exists simply in solution in the water can thus be expelled, yet a portion of carbonic acid escapes at the same time from the bicarbonates in solution. The earthy bicarbonates lose half of their carbonic acid, and are converted into simple carbonates. As to the quantity of carbonic acid which comes from the carbonates of alkalies, it cannot be determined with accuracy, because their solutions lose more or less carbonic acid, according to the length of time during which they are boiled, or according to the pressure of the column of water or of mercury which the gas has to traverse before it can escape.

\* The carbonic acid which is disengaged from a mineral water by a prolonged ebullition, is ordinarily reckoned in the results of the analysis, under the name of free or half combined carbonic acid, which expression has not a very clear sense, or does not quite agree with the fact, as may be perceived from what has been said above.

\* As it is not important to determine in the gaseous state, the carbonic acid which can be expelled from mineral waters by boiling, since the volume produced in several successive experiments is never exactly the same, it is best to determine the whole of this acid in solution, by precipitating it by means of a solution of a chloride of calcium or of barium.

\* The second of these two salts (chloride of barium,) has so many advantages over the other that it should always be used in preference.

\* A given volume of the mineral water is to be treated by pure ammonia, and a sufficient quantity of chloride of barium is added to it. The bottle containing the whole is then hermetically closed, shaken, and left at rest for several hours. The precipitate contains the whole of the carbonic acid, combined with the baryta, and also the whole of the sulphuric acid of the mineral water, in the state of sulphate of baryta, and, lastly, the substances contained in the mineral water, which separate in an insoluble state by evaporating the liquor. (After the above precipitate has completely settled), The supernatant liquor is poured on a filter, hot water is added to the deposit, the bottle is again corked up, and left at rest until the deposit has completely settled at the bottom, and this operation is repeated several times (page 543). Lastly, the precipitate is thrown on a filter, and washed with hot water until, by mixing a little of the filtered liquor with some nitric acid, it is no longer rendered turbid by testing with nitrate of silver. In filtering the liquids, the access of the atmospheric air must be carefully avoided. After having dried the precipitate, it is ignited and weighed; the insoluble matter which is deposited by the evaporation of an equal or proportional volume of the mineral water, is ignited and deducted from this weight, and the quantity of the sulphate of baryta formed by the sulphuric acid contained in the mineral water is likewise deducted. The remainder is carbonate of baryta, from which the quantity of carbonic acid may be easily calculated.

\* If, instead of chloride of barium, a solution of chloride of calcium is employed to precipitate the carbonic acid, many difficulties are met with. The carbonate of lime precipitated often adheres to the sides of the glass with so much force that it cannot be detached by any mechanical means, so that it is necessary to dissolve it in muriatic acid, and to precipitate the lime a second time by carbonate of ammonia. This does not so easily take place with carbonate of baryta. This latter salt may be ignited without losing any of its carbonic acid, whilst, in calcining the carbonate of lime, the precautions which have

been mentioned (page 19) must be observed. Lastly, a solution of chloride of calcium does not precipitate the whole of the sulphuric acid in the state of sulphate of lime; it is necessary, therefore, to perform a separate experiment to determine the quantity of sulphate of lime in the precipitate, that is to say, it must be treated by muriatic acid and alcohol, which leaves the sulphate of lime in an insoluble state, which must be well washed with weak alcohol.

\* The analysis becomes a little more complicated when the mineral water is combined with phosphoric acid also, for the precipitate in that case contains phosphate of baryta besides. This case, however, is rare; and when the mineral water contains carbonate of lime, the quantity of the phosphate of alkali cannot but be extremely small, and may be neglected. But as the quantity of the phosphate of alkali has been determined before, the corresponding quantity of the phosphate of baryta in the precipitate may be calculated therefrom.

\* After having ignited the baryta precipitated, the quantity of carbonic acid which it contains may be immediately determined by decomposing it in a glass tube filled with mercury (page 539).

\* The most difficult point in this analysis is to determine accurately a volume of the mineral water, when it contains a very large proportion of carbonic acid without losing a certain quantity of the gas pending that determination. In effect, when the water comes in contact with the air, the latter, combining with it, expels a small quantity of carbonic acid, wherefore, when the mineral water is poured in the usual way (page 642), there is a considerable loss of carbonic acid.

\* The best is to determine this acid at the spring, and, according to Liebig, the volume of the water to be experimented upon is determined as follows:

\* A bottle, having a somewhat wide mouth is taken and a known volume of a mixture of solution of chloride of barium

and ammonia is introduced into it, and it is closed with a cork perforated with two holes, to which two glass tubes of an equal diameter, and which project out of the cork, the one about half an inch, the other about four inches, are adapted. The tubes should also project a little from the cork inside the bottle, the shortest tube about two inches, the other one inch. When this apparatus is plunged into the spring, the water penetrates into the bottle by the shortest tube outside, and the air escapes through the other.

\* It is clear that the water ceases to enter into the bottle as soon as the level of the water reaches the orifice of the shortest tube internally, and stops that orifice. According to the depth at which the bottle is plunged, the water now ascends into the tube externally the longest, and when the bottle is brought up, a portion of it flows out from the shortest tube, the liquid becoming level in the two tubes, which may be obviated, since the operator can always observe the ascension of the water in the longest tube.

\* The volume of the water is easily obtained by marking the height of the liquid in the bottle, by marking the bottle with a file at that point, and, from the volume obtained, the operator deducts that of the solution of chloride of barium mixed with ammonia, which had been previously put in the bottle.

\* Instead of the process just described, the following may also be employed:—The operator takes a glass pipette, or a glass bulb, a cylinder, &c., capable of containing about one pound of liquid, with two openings opposite each other, to which glass tubes are soldered; the one two inches long and one quarter of an inch wide; the other, from six to eight inches long, is narrower. This apparatus is plunged into the spring, so that one of the openings is downwards whilst the other is turned vertically upwards. As soon as the upper aperture is below the level of the water, it is closed with the thumb, and the other is corked up with a cork, traversed by a narrow glass tube. This must be done whilst the apparatus is under water, after which the apparatus



may be brought out without fear of the water running from it, even though the narrow glass tube underneath is left open.

\* This determined volume of the mineral water is now to be mixed with the solution of chloride of barium, to which ammonia has been added; this is done by pouring the quantity of this solution necessary to effect the decomposition into a wide bottle, which must be just so high that the narrow tube of the pipette filled with the mineral water plunges only a short distance under the liquid, and yet reaches the bottom of the bottle. On lifting the thumb from the upper orifice of the pipette, the mineral water runs into the bottle, and mixes with the solution of chloride of barium; the pipette is then filled with distilled water, to which a few drops of ammonia have been added, and this liquid is allowed to flow in the water of the bottle. The volume of the water is known by measuring the pipette.

\* Of course this operation may be repeated several times, and three or four volumes of water may thus be mixed with the solution of chloride of barium.

\* The bottle containing the mixture is closed until the precipitate has deposited, and the operator proceeds as was said above.

ANALYSIS OF MINERAL WATERS WHICH CONTAIN FEW CARBONATES OF ALKALIES, AND IN WHICH THE EARTHS ARE LESS IN THE STATE OF CARBONATES THAN (FOR THE MOST PART) IN THE STATE OF SOLUBLE SALTS (*Eaux Salines*).

\* Waters of this description contain less free carbonic acid or other volatile constituents, the quantities of which it is not so important to determine. In order to take their specific gravity, or to measure promptly and accurately a certain quantity of it, the same bottles as those which have been described before may be employed.

\* The course of the analysis of these mineral waters might also resemble that which has been described, but ordinarily alcohol is employed to separate the soluble salts from those which are

not so, and which are insoluble in this menstruum, a method which, as will be shown farther on, should not be recommended.

\* When the operator wishes to determine the quantity of the solid constituents in the whole, he evaporates to dryness a given portion of the mineral water, observing the precautions mentioned (page 642.)

\* During this experiment, if the water contains chloride of magnesium, this salt undergoes a partial decomposition under disengagement of muriatic acid. When the quantity of the fixed constituents has to be determined, the residuum must be exposed to a dark red heat in contact with the air, until the extractive matter of the water is destroyed, which is exceedingly difficult when that matter is abundant. As the whole of the magnesia is ordinarily in the state of chloride of magnesium in the mineral water, the operator calculates how much chloride of magnesium corresponds to the magnesia left in the insoluble residuum. But in operating thus, all error in the determination of the magnesia is taken account of as chlorine, and it is impossible to arrive very accurately at the quantity of the fixed constituents contained in the water, especially as the magnesia separated from the chloride of magnesium by heat is not pure, and may contain chlorine.

\* When the mineral water contains alumina salts, they lose also part of this acid, and become insoluble in water.

\* According to Mohr, the quantity of the fixed constituents may be exactly determined by adding to the water during the evaporation, a weighed quantity of fused carbonate of soda. This salt, whilst it is dissolving, precipitates the lime, and the magnesia in the state of carbonates; the water thus acquires the composition of an alkaline mineral water, and may be analysed in the same manner as the latter. The quantity of carbonate of soda added, must be sufficient to decompose the chloride of magnesium and the chloride of calcium completely.

The dried and ignited mass gives, after extracting the excess of carbonate of soda, the quantity of the fixed constituents of the water. It should be recollected, that in calcining the dry mass, the carbonate of magnesia will have lost all its carbonic acid. If the saline water holds carbonates of earths and of protoxyde of iron in solution, these salts should be separated previous to adding carbonate of soda; that is, when it is wished to determine them separately. Otherwise, after having added the carbonate of soda, the whole is evaporated to dryness.

\* Instead of this method, the quantity of the fixed constituents, according to Liebig, may be determined by adding to the mineral water a little muriate of ammonia. The whole is then carefully evaporated to dryness, and the dry residuum is ignited and fused. The fused mass is weighed. The addition of muriate of ammonia prevents the chloride of magnesium from being decomposed during the evaporation and ignition. If the saline mineral water contains no carbonates, the weight of the ignited mass gives exactly the quantity of the fixed constituents of that water. In the contrary case, the carbonates are converted into metallic chlorides, and the operator may determine by this process the quantity of the chlorides by evaporating the water almost to dryness, treating the residuum by water, separating the insoluble carbonates, and adding muriate of ammonia to the solution, evaporating again to dryness, and igniting the dry mass. From the weight of the latter the operator must deduct that of the sulphates obtained by calculating from the quantity of the sulphuric acid found, that of the sulphate of soda or of the sulphate of lime, (if this last substance is present).

\* When saline mineral waters do not contain a large proportion of metallic chlorides, the analysis may be proceeded with, as for that of alkaline waters. But the metallic chlorides are sometimes so abundant that a portion of the water must be devoted to the determination of the chlorine, because with the quantity of liquid which is necessary for the determination of

the substances which are not abundant, the precipitate of chloride of silver produced would be too considerable.

\* The method which consists in separating by means of alcohol from the fixed constituents of the saline water, the salts which are very soluble from those which are sparingly so, and which are insoluble in alcohol, is not to be recommended, and can be employed only in a small number of cases, when the proportion of chloride of magnesium in the water is very slight. This method is briefly as follows :—

\* *a.* The residuum of the mineral water which has been evaporated without addition of carbonate of soda or of muriate of ammonia, is digested for a long time with about six times its quantity of alcohol of specific gravity 0·833. The action of this menstruum upon the saline mass is facilitated by carefully pulverising the latter before the treatment. The vessel is then covered with a plate of glass, in order to prevent the alcohol as much as possible from evaporating.

\* The alcoholic solution is then passed through a weighed filter. The capsula is washed with alcohol, so as to remove all the portions which have not dissolved, and which are likewise thrown on the filter, taking care to detach all that which may adhere to the capsula, either with the feather of a quill or with the finger. The undissolved portions are washed with hot alcohol until the latter ceases to dissolve any thing.

\* The alcohol dissolves principally the combinations of chlorine which exist in the mineral water, such as, for example, chloride of calcium, chloride of magnesium, (provided it has not been rendered insoluble in this menstruum by calcining it too strongly) chloride of potassium, and chloride of sodium.

\* Both chlorides of potassium and of sodium being much more difficult to dissolve in alcohol, especially when the latter is very strong, than chloride of calcium and chloride of magnesium, it is customary to treat first the fixed residuum of the mineral water with absolute alcohol, in order to remove only the chloride of calcium and that of magnesium, and to leave

the chloride of potassium and that of sodium, which are subsequently dissolved with alcohol, of specific gravity 0.833. But in this operation a small portion of chloride of sodium is always dissolved simultaneously with the chlorides of calcium and of magnesium, which it is impossible to prevent.

\* If the residuum of the mineral water has not been calcined, but if the latter has been carefully evaporated to dryness at a gentle heat, the alcohol dissolves also a great portion of the organic substance which it contained.

\* *b.* The alcoholic solution of the salts is carefully evaporated to dryness, and the quantity of the fixed residuum (when chloride of magnesium is not present) is determined. This residuum is next treated by water, which dissolves it completely, when the chloride of magnesium dissolved by the alcohol has not been partially decomposed by drying too strongly. Often, also, portions of organic matter, of a resinous kind, are left, when they have not been burnt during the ignition of the fixed residuum produced by the evaporation of the mineral water.

\* A little nitric acid is poured in the solution, in order to render it acid, and a solution of nitrate of silver is added, in order to precipitate all the chlorine in the state of chloride of silver. If the mineral water contains a combination of iodine or of bromine, iodide and bromide of silver will have been precipitated with the chloride of silver, and the two salts may then be separated from each other.

\* The excess of nitrate of silver poured in the liquor is afterwards precipitated in the state of sulphuret of silver by a current of sulphuretted hydrogen. The liquor separated from this precipitate by filtering, is heated for a long time in order to expel the sulphuretted hydrogen which it holds in solution, it is then saturated by ammonia, and by means of a solution of oxalate of ammonia the lime is precipitated and determined.

\* The liquor filtered from the oxalate of lime is evaporated to dryness, and the dry residuum is calcined in a platinum crucible until the nitrates are completely decomposed. It is necessary,

after the ignition, to put a small piece of carbonate of ammonia into the crucible and to ignite it strongly again (page 44). The residuum consists of magnesia, of carbonate of soda and of potash, (if this substance is contained in the mineral water).

\* The dried and weighed residuum is treated by water, which dissolves the alkaline carbonates, and leaves the magnesia. The quantity of the latter is first determined, the alkalies, if both exist in the water, are separated from each other in the manner indicated (page 7).

\* *c.* The portion of the dry residuum of the mineral water which refused to dissolve in alcohol (at *a*) is treated by hot water until the latter ceases to dissolve anything. The water dissolves principally the sulphates, such as sulphate of soda, and often, also, sulphate of potash, sulphate of magnesia, and sulphate of lime. If the latter be abundant a large quantity of water is required to dissolve it.

\* In order to render the solution acid, acetic acid is poured into it in sufficient quantity, so that by supersaturating it with ammonia no magnesia will be precipitated. To the liquor containing a slight excess of ammonia, a solution of oxalate of ammonia is added in order to precipitate the lime.

\* The liquor separated from the oxalate of lime is rendered acid by acetic acid, and then, by pouring into it a solution of acetate of baryta, the sulphuric acid is precipitated in the state of sulphate of baryta, the quantity of which is determined.

\* The solution separated from the sulphate of baryta by filtering is evaporated to dryness, and the dry residuum is calcined until the acetic acid which it contains is destroyed. The calcined mass is treated by water, which dissolves the carbonates of alkalies, and leaves the magnesia and carbonate of baryta. The solution of the alkalies is evaporated to dryness in order to determine the quantity of alkali, and they are separated from each other by the method indicated (page 7).

That which water has not dissolved is supersaturated with dilute sulphuric acid. The sulphate of baryta produced is

separated by filtering, and thrown away, from the solution of the sulphate of magnesia which is evaporated to dryness, and the quantity of this latter salt is determined.

\* *d.* The residuum which has not been dissolved by either alcohol or water is treated by nitric acid, which ordinarily leaves silicic acid. The whole is evaporated to dryness in a platinum capsula, the dry mass is moistened with nitric acid, and some time afterwards it is treated by water, which leaves an undissolved residuum of silicic acid. The nitric acid solution filtered from the silicic acid may contain magnesia, lime, and sometimes also strontia, which existed in the residuum in the state of carbonates. When the mineral water contains much chloride of magnesium, and the residuum is strongly ignited, the magnesia often exists in considerable quantity in the nitric acid solution, in which case the latter contains muriatic acid also. In certain cases the nitric acid solution contains also phosphoric acid, fluoride of calcium, alumina (either when in combination with phosphoric acid, or when the salts of alumina of the mineral water contained in the dry residuum have been strongly ignited), peroxyde of iron, and sesquioxide of manganese. This solution is examined in the same manner as the nitric acid solution of the insoluble residuum of the mineral water containing carbonic acid, according to the method which has been explained (page 650, at F.)

\* This treatment of the mineral water by alcohol presents great difficulties, and yet does not yield accurate results. It is better to employ water only to separate the fixed residuum into soluble portions and insoluble portions, which, however, requires a very large quantity of water, if sulphate of lime is in abundance. The quantities of the chlorine of the sulphuric acid, and of the bases contained in the aqueous solution, are afterwards determined in the manner described (page 646). If the quantity of sulphate of lime is great, it is best not to evaporate the solution, and at once to determine the constituents.

\* In indicating the constituents of water from a salt spring or from sea-water, they are frequently named as they are obtained in the analysis, executed as has been just described; hence the discrepancies which are observed between the various analyses of a same water. Thus we often read that, according to Murray sea-water contains sulphate of soda and chloride of magnesium and chloride of calcium, though, in all probability, these salts must mutually decompose each other, even in dilute solutions. It is, in effect, impossible to ascertain with accuracy the mode of combination of the constituents of the two salts when their solution produces no insoluble or sparingly soluble precipitate. But if we admit that, in saline solutions, the salts are contained in the state of simple salts, and not in that of double salts, or of other combinations, the most probable supposition is, that most generally the salts exist in the solution juxtaposed, and in the state in which they separate by crystallisation when the water is evaporated spontaneously or by means of a temperature as gentle as possible. In such a case the least soluble salt separates first. The reasons adduced by Murray in favour of his hypothesis are untenable.

\* When saline waters are left to evaporate slowly during summer, several precipitates take place in the following order: first, sulphate of lime, then chloride of sodium, and lastly sulphate of magnesia, in a greater or less state of purity, partly mixed with chloride of sodium, whilst chloride of magnesium, which is the most soluble of the salts, remains in the mother water. Sulphate of soda is precipitated by spontaneous evaporation only when the acid and the soda are more abundant than the magnesia and chlorine.

\* Bonsdorf showed that by evaporating sea-water at the ordinary temperature, more sulphate of lime may be obtained than had been hitherto admitted.

\* It is true that, under the influence of different temperatures, the combinations undergo remarkable changes in saline solutions, but they are generally referable to this, that the salts are not uniformly soluble at various temperatures. The most



extraordinary changes are those which a mixture of chloride of sodium and of sulphate of magnesia undergo. When these two salts are dissolved in a sufficient quantity of water, and the latter is left to evaporate at the ordinary temperature, at least in summer, there is a separation of sulphate of magnesia and of chloride of sodium, but in such a way that if the liquor contains much chloride of sodium, and little sulphate of magnesia, a portion of chloride of sodium first falls down, then sulphate of magnesia is deposited, whilst the water still contains chloride of sodium, because at the temperature of summer, sulphate of magnesia is nearly as soluble as chloride of sodium. If the temperature be lowered to  $0^{\circ}$  cent. ( $32^{\circ}$  Fahr.), or raised to above  $50^{\circ}$  cent. ( $122^{\circ}$  Fahr.), sulphate of soda is deposited, and chloride of magnesium formed, because at  $0^{\circ}$  cent., sulphate of soda is the least soluble of the four salts which may be contained in the liquor [chloride of sodium, sulphate of magnesia, sulphate of soda, and chloride of magnesium], and at a temperature above  $50^{\circ}$  it separates in the anhydrous state. It is, therefore, right to admit that, at the ordinary temperature, sulphate of magnesia and chloride of sodium exist simultaneously in that very state.

\* In the analysis of sea-water, of saline waters, &c., according to the method formerly employed, and which consisted in evaporating the water and treating the residuum by alcohol, some chemists have indicated sulphate of soda as existing in that water, because this substance was found by them amongst the sulphates insoluble in water, whilst most other chemists could obtain none. Lavoisier, in his analysis of sea-water taken at Dieppe, and Lichtenberg in that of the Baltic, mention sulphate of soda, chloride of magnesium, sulphate of magnesia, and chloride of sodium, among the constituents, because they obtained these salts immediately; whilst Vogel, in several samples of sea-water, Link and Pfaff, in that of the Baltic, could not detect the presence of sulphate of soda in operating in the same manner.

\* Grotthuss attributes these discrepancies to this circumstance that sulphate of magnesia and chloride of sodium, when boiled in alcohol, are gradually decomposed into chloride of magnesium and sulphate of soda. This decomposition, doubtless takes place, but it is only to a slight extent, and it further requires a strong and prolonged ebullition, which can hardly be admitted to have been the case in the said analysis. The principal cause of the presence of the sulphate of soda found in sea-water, is unquestionably due to the evaporation of the water, having been performed by two strong, perhaps by a boiling heat. On this account also, the deposit which is formed in the pans in which the water of salt-springs is evaporated consists principally of sulphate of soda. The chemists who have evaporated sea-water at a temperature below 50° cent., could not obtain sulphate of soda.

\* When in the qualitative analysis of a mineral water, or rather of a well-water, nitric acid has been found, the determination of this acid is very difficult. After having treated by alcohol the residuum of the evaporation of the water, the nitrates are ordinarily dissolved by this reagent; if the water, however, contains potash, the residuum undissolved by the alcohol contains nitrate of potash.

\* After having determined in the salts of the water, the bases and the quantity of sulphuric acid and of chlorine, and calculated how much base the latter require to form neutral salts, the quantity of the nitric acid may be found by admitting that the excess of the bases is combined with it. If the operator wishes to determine its quantity in an immediate manner, he may take a solution of the salts, precipitate the chlorine by a solution of nitrate of silver, separate the chloride of silver, evaporate carefully the filtered liquor, and treat the concentrated solution by sulphuric acid, as was said (page 618).

## ANALYSIS OF SULPHUROUS MINERAL WATERS.

In the analysis of the mineral waters which contain free sulphuretted hydrogen, or a metallic sulphuret forming a sulphhydrate, when treated by sulphuretted hydrogen (*eaux hépatiques*) the operator begins by determining the quantity of the sulphur which exists both in the sulphuretted hydrogen and in the metallic sulphuret. This is done by pouring in a known quantity of the mineral water a solution of a metallic salt, capable of forming an insoluble metallic sulphuret. A solution of nitrate of silver, or of acetate of lead, or of protosulphate of copper is ordinarily used for the purpose.

\* When solution of nitrate of silver is used for the purpose of determining the quantity of sulphur contained in the mineral water, an excess of ammonia must be added to the silver solution, which prevents chloride of silver from being precipitated with the sulphuret of this metal. If combinations of iodine are present, iodide of silver is precipitated, when ammonia alone has not produced a precipitate in the mineral water. If, however, ammonia alone can produce a precipitate in the mineral water, this reagent should be added to the latter before pouring the solution of nitrate of silver, and the precipitate produced should be first separated by filtering, after which the sulphuret of silver is precipitated by the solution of the nitrate of this metal. The sulphuret so produced is allowed to settle well, it is then collected on a weighed filter, and its quantity is determined, from which that of the sulphur contained in the mineral water is calculated.

\* If a solution of acetate of lead, to which free acetic acid has been added, is employed to determine the sulphur, sulphate of lead, and even chloride of lead are precipitated along with sulphuret of lead.

\* If a solution of protosulphate of copper is employed, nothing but sulphuret of copper is precipitated, provided a free acid

has been added to the copper solution. But as sulphuret of copper absorbs easily a little oxygen whilst it is filtering, its quantity cannot be as accurately determined as that of sulphuret of silver, owing to which the solution of nitrate of silver is preferable for the purpose. A solution of protochloride of copper (*chlorure cuivrique*) is, however, preferable to all; the sulphuret of copper thus obtained is completely oxydised by fuming nitric acid, and the sulphuric acid thus produced is determined by a solution of a salt of baryta.

\* After having thus determined the proportion of sulphur in a given quantity of mineral water, another portion of the latter is now devoted to the determination of the fixed constituents which are thus determined by the methods which have been described before. During the evaporation, the soluble metallic sulphuret contained in the mineral water is decomposed, which circumstance must be taken into consideration.

\* The mineral waters which contain carbonates of alkalis contain no free sulphuretted hydrogen, but a soluble metallic sulphuret. If, however, the mineral water contains bicarbonate of alkalis, carbonic acid, and a soluble metallic sulphuretted hydrogen gas is disengaged along with the carbonic acid when it is heated in a retort.

\* With the mineral waters which contain much carbonic acid and free sulphuretted hydrogen, a gas escapes generally from the spring, sometimes in such a quantity that the water seems to be in constant ebullition. In order to examine this gas it must be collected at the spring in a graduated glass tube. The tube is first filled with the water of the spring, its orifice is then plunged under the level of the water, and the air-bubbles which disengage are collected. When it is filled with the gas its orifice is closed with the finger, and opened over mercury. The sulphuretted hydrogen, and carbonic acid, are then absorbed by hydrate of potash, and the remaining gas, which contains much nitrogen is examined.

\* If the quantity of sulphuretted hydrogen contained in this gaseous mixture is so slight that its volume cannot be accurately determined by absorption, a large bottle must be taken of a known capacity, and filled with the gaseous mixture as we have just said; the opening is then closed with the finger or with a glass stopper, and it is opened under a solution of nitrate of silver, or of acetate of lead, to which acetic acid has been added. After some time, when the gas has cooled, for it has a high temperature since it generally proceeds from hot springs, as much of the metallic solution penetrates into the bottle as is necessary to absorb the small quantity of sulphuretted hydrogen. The bottle is then closed up, shaken with the solution, and the quantity of sulphuret of silver or of lead produced is determined, from which the volume of the sulphuretted hydrogen gas is calculated.

\* Some mineral waters contain also a soluble metallic sulphuret, and a hyposulphite resulting from the slow oxydisation of the metallic sulphuret. After having determined the quantity of sulphur contained in such water by means of a solution of silver, the hyposulphite will have been destroyed with formation of sulphuret of silver, and of a sulphate. The quantity of the sulphur of the mineral water may then be determined by means of a zinc-solution, which produces sulphuret of zinc, and afterwards that of the hyposulphurous acid by means of a solution of silver, (page 417).

\* I have said, in the first volume of this work, what is the process to be followed for the detection of some rare constituents existing in certain mineral waters. The quantitative determination may be performed by the methods which have been exposed in this volume.

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Note by M. E. Peligot.

\* M. Du Pasquier indicated a simple and practical method of determining the sulphuretted hydrogen in a free or in

a combined state, existing in solution in a mineral water. This method is grounded upon the property which iodine possesses of precipitating sulphur immediately from these combinations, and of combining with the hydrogen. A given weight of iodine is dissolved in alcohol, and a certain volume of the solution is introduced into an instrument called by M. D. Pasquier a sulphydrometer.<sup>1</sup> This instrument is a pipette, or graduated tube, terminated by a capillary aperture whilst the other end is closed with a cork; the tube being filled with the tincture up to 0° of the graduated scale, the liquor falls drop by drop upon removing the cork.

\* To use the sulphydrometer proceed as follows:—Pour in a porcelain capsula a given quantity of the sulphurous water to be analysed, and add thereto a few drops of a very clear solution of starch, and the solution of iodine of a known strength is poured into the liquor thus prepared. The whole is stirred, and the iodine solution is poured into it until the liquor begins to have a blue tinge, which indicates that all the sulphuretted hydrogen is decomposed. The operator thus reads on the tube how much tincture has been used, and as he knows the quantity of iodine which it contains, the quantity of sulphuretted hydrogen which has been decomposed is easily calculated. It is advisable to prepare the liquor, so that each degree represents one centigramme of iodine, and each tenth of a degree or milligramme.

\* This method, according to Berzelius, is not accurate. The iodine in dissolving in alcohol, reacts upon the elements of the substance, hydriodic and other iodated products are formed, and it is only the free iodine, dissolved by this acid, which acts in the sulphydrometer. Moreover, it is well known that in the course of time the free iodine combines with the elements of the solvent. Berzelius recommends to use an aqueous solution of chloride of potassium or of sodium instead of alcohol.

\* Whatever be the liquid employed to dissolve the iodine, the

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<sup>1</sup> Mémoire sur la Construction et l'Emploi du Sulfhydromètre, Paris 1841, 8<sup>e</sup>. *Bulletin de l'Académie de Médecine*, t. vii. p. 728.

experiment, as just described, is insufficient for two reasons: 1st, it does not indicate whether the mineral water contains free sulphuretted hydrogen, or alkaline sulphurets in solution, or a mixture of these bodies; 2nd, it does not even indicate with accuracy the sulphur contained in the state of sulphuretted hydrogen or of sulphuret. When the water, having remained for some time in contact with the air, contains a certain quantity of hyposulphite, which has resulted from the action of the oxygen of the air upon the sulphurets in solution, it is known that the hyposulphites absorb iodine and are transformed into iodides and bisulphuretted hyposulphates.

\* The mineral water, according to M. Henry, may be agitated in a completely filled bottle with some powder of pure silver until the odour of sulphuretted hydrogen has disappeared. The operator having determined by a first trial with the sulphydrometer the total proportion of sulphur contained in this gas and in the sulphurets, a second operation gives that of the sulphur of the sulphurets, and the difference indicates the proportion of sulphuretted hydrogen.

\* In order to determine separately the sulphur of the hyposulphites, M. Henry boils a given quantity of the sulphurous water with bicarbonate of potash, the ebullition and the carbonic acid expel, in the state of sulphuretted hydrogen, the sulphur which existed already in that state, or in that of sulphuret. When this water no longer precipitates the ammonia-nitrate of silver, the sulphydrometer may then be used, for it will then indicate only the sulphur of the hyposulphites.

\* Lastly, M. Du Pasquier, taking a complicated case of a mineral water, containing simultaneously sulphur in the state of sulphuretted hydrogen, of sulphurets of alkalies, and of hyposulphites, proposed the following process:—The operator begins by determining, by means of the test iodine-liquor, the collective quantity of sulphur contained in these three states. He then

adds to a fresh quantity of mineral water some neutral sulphate of zinc, until the sulphur of the sulphurets and of the sulphuretted hydrogen is completely precipitated;<sup>1</sup> the liquor is then filtered, the deposit of sulphuret of zinc is washed, and the water used for the washing is mixed with the filtered liquor, and, lastly, the sulphur which is contained in the liquor, now in the state of hyposulphite, is determined by the sulphydrometer.

#### DETERMINATION OF THE ORGANIC MATTER OF THE MINERAL WATERS.

According to Berzelius, this matter consists, in a great number of cases, of crenic and apocrenic acids, which are partly in solution in the water and combined with alkalies, and partly contained in the deposit of certain waters mixed with peroxyde of iron. They may be separated from the mineral water in the following manner:—Acetic acid is added to the water until it becomes sensibly acid, a solution of acetate of copper is then poured in, as long as a brown precipitate is produced. An apocrenate of copper is thus formed, which precipitates whilst the crenate of copper remains dissolved in the free acetic acid. The apocrenate of copper is washed with a small quantity of water only, for a larger quantity might dissolve a little of it. To the filtered liquor a solution of carbonate of ammonia is added, until the acetic acid is completely saturated. A very slight excess of acetic acid is not objectionable. Crenate and acetate of copper are precipitated. When the mixture has been slowly heated to 50° cent., the crenate of copper precipitates better; an excess of acetate of copper is likewise necessary. As long as the filtered liquor is greenish, and not of a pure blue colour, it still holds crenate of copper in solution, which may be precipitated by carefully adding carbonate of ammonia, and heating the liquor. The crenate of copper is well washed, mixed with a little water, and then decomposed by sulphuretted hydrogen, otherwise the

<sup>1</sup> Sulphate of zinc does not appear to be very suitable for absorbing the sulphuretted hydrogen.—ED.



sulphuret of copper which separates is not black, but of a brownish colour, and if it is filtered immediately the liquor passes through the filter with a brown tinge. But if the whole be left at rest for twenty-four hours in a closed bottle, the sulphuret of copper may be collected on a filter. Yet the greater the quantity of water employed the more difficultly does the sulphuret separate from the liquor. It still contains a small quantity of apocrenic acid, which may be extracted by means of carbonate of alkali. The liquor filtered from the sulphuret of copper is evaporated in vacuo over sulphuric acid; there remains crenic acid, the weight of which may then be determined.

\* The apocrenate of copper is treated in the same manner by sulphuretted hydrogen gas, in which case it is still more difficult to separate the sulphuret of copper from the liquor.

\* In order to separate the crenic and apocrenic acid from the deposit of peroxyde of iron which certain mineral waters form in contact with the air, this deposit must be boiled with a solution of potash until it has lost all cohesion, and assumed the appearance of a precipitate of peroxyde of iron, which requires that it should be boiled for several hours. If the deposit were only put in digestion with the solution of potash, the decomposition would be very far from being complete; yet even after a long ebullition, the peroxyde of iron is not totally separated from the two acids. After having acidified the filtered liquor by acetic acid, the two acids are separated by the means which have been indicated.

#### DETERMINATION OF HYDROGEN IN GASEOUS COMPOUNDS.

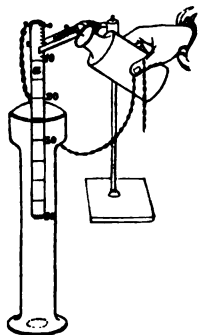
When hydrogen is mixed in the gaseous state with other gases, the volume, and consequently the quantity, is determined by the diminution of volume which takes place when a given quantity of oxygen being added to the gaseous mixture, the whole is exploded. This diminution of volume, if oxygen remains, indicates the volume of the hydrogen gas. The latter forms the two-thirds of the volume of the gas which has disappeared, and has been converted into liquid water.

The instrument used for this experiment consists of a thick glass tube a foot or a foot and a half long, closed at one end and open at the other; its diameter needs not be more than about a quarter of an inch. Near the closed extremity two wires of iron or of platinum pass through the glass; these wires are hermetically luted, or if the glass is thin, they may be soldered to it. These wires are placed opposite each other in the interior of the tube, and they must come near each other but without touching; the extremity outside of the tube may be rounded. The internal capacity of the tube is divided into equal parts, when the experiment has no other object than finding the relative proportions of the mixed gases; otherwise the divisions can be arbitrary, and especially if the weight of a gas has to be calculated from its volume. The unit measure is a cubic centimetre.

To analyse the gaseous mixture, fill the tube with mercury, taking care that no small bubbles of atmospheric air adhere to the sides, to avoid which the tube should not be at first quite filled, and it should then be shaken, and the sides should be rubbed up and down with the feather of a quill. The tube is then completely filled with mercury, and plunged in a mercurial trough, and a small quantity of the gas intended for examination is made to ascend through the mercury into it. The tube is then sunk into the trough until the metal is externally level with the interior, and the volume of the gaseous mixture is accurately noted. In order to maintain the tube in the mercury, it is pinched between a clamp, which can be screwed at various heights on a wooden stand.

This being done, the mixture of oxygen and of hydrogen is inflamed by means of an electric spark. The best way of performing this experiment consists in coiling one of the extremities of a chain or of a metallic wire round one of the wires outside of the glass tube, or to hook it thereto, and to apply the other extremity to the exterior coating of a charged Leyden jar. The knob of the bottle being now brought into contact with the opposite wire, an electric spark passes from one wire to the other, through the gaseous mixture, which it inflames.

\* As a mixture of hydrogen and of oxygen gases dilates excessively at the moment it is deflagrated, the volume of the



gaseous mixture to be examined must not exceed about one third of the capacity of the glass tube in which the combination takes place. If this volume were more considerable at the moment of the inflammation by the electric spark, the dilation of the gases might expel a portion of it out of the tube, which of course would vitiate the experiment. The explosion may also be so violent that the glass tube, if not pinched sufficiently tight in the clamp, will be tilted on one side, and a portion of the mixture escape, and be replaced by atmospheric air. It is therefore necessary to plunge it to the bottom of the mercurial trough.

If the gaseous mixture consisted of hydrogen and oxygen in the proportion of two volumes of the first, and more than one volume of the second, the exact excess of the latter gas, above half the volume of the hydrogen gas, remains behind after the detonation. The tube is then plunged in the mercury until the level of the metal be the same inside and outside the tube, and the oxygen remaining is measured. As the gas which has disappeared was composed of two volumes of hydrogen and one volume of oxygen, the proportion of the gases which were mixed together is easily found. If, for example, the mixture of oxygen and hydrogen was twelve volumes, and three volumes of oxygen

remained after the deflagration, the mixture consisted of six volumes of hydrogen and six volumes of oxygen.

If the gaseous mixture consisted of two volumes of hydrogen and less than one volume of oxygen, the remaining gas is hydrogen. Its volume is measured, and from the quantity of the gaseous mixture which has disappeared, that of the hydrogen and of the oxygen is calculated. If, for example, the mixture of oxygen and of hydrogen gas under examination was twelve volumes, and three volumes of hydrogen remain after deflagration, the mixture consisted of nine volumes of hydrogen and three volumes of oxygen.

When, however, the operator does not know whether the gas which remains after the deflagration is oxygen or hydrogen, the volume is determined, and oxygen is added thereto, but not less than half the volume of the remaining gas. The electric spark is then passed through the mixture. If no diminution of volume follows, it is a proof that all the gas is oxygen; if a diminution of volume is perceived, it is a proof that the remaining gas contained hydrogen still. If, for example, the mixture of hydrogen and of oxygen experimented upon was twelve volumes, and three volumes of gas remained after deflagration, and the operator does not know whether they consist of hydrogen or of oxygen, he adds thereto one volume and a half of oxygen, and the electric spark is passed through the mixture. If the gas disappears entirely, the residuum of the first deflagration was hydrogen, and the twelve volumes of the gaseous mixture experimented upon consisted of nine volumes of hydrogen and three of oxygen.

\* Oxygen gas is introduced into the glass tube as follows :— A little chlorate of potash is put into a tube blown into a bulb at one of its ends, and the other extremity is drawn out to a point and bent at the same time, so that it may be used as a small retort. The chlorate of potash is then fused by the flame

of a small spirit-lamp, and when, from the rapidity of the disengagement, the operator knows that pure oxygen is evolved, the point of the tube is fused, so as to seal it, and the small retort is allowed to cool. When the operator wishes to add a little pure oxygen to a gas, he breaks the point of the retort under mercury, and he proceeds to fuse the chlorate of potash, the extremity of the tube of the small retort being placed under the graduated tube, so that the oxygen disengaged may ascend into it.

It should be remarked, that a mixture of oxygen and of hydrogen cannot be inflamed by the electric spark when the volume of one of the gases exceeds much that of the other. If, for example, the gaseous mixture contains, according to Davy, fourteen volumes, and according to Gay Lussac and Humboldt, nine volumes and a half of oxygen for one only of hydrogen, or according to Davy, twenty-six volumes of hydrogen for one only of oxygen, the mixture does not detonate. I shall indicate farther on what method should be employed in such a case.

As it is advisable in rigorously accurate analysis not to operate upon too small quantities of gas, a tube of a different form, which was proposed by Metscherlich, may be used. It differs from the other in this, that it has two holes near its open extremity, placed opposite to each other, and large enough to receive a glass stopper, which, at the same time, closes the tube hermetically. The tube may be filled with the gaseous mixture up to the stopper, and the electric spark may then be passed through it without fear of its breaking. This tube can hardly be used for any other analysis besides that of atmospheric air, because it is difficult to introduce other gaseous mixtures into it.

According to Döbereiner, in such experiments the combination of the two gases may be effected by finely divided platinum instead of by the electric spark, the result of the combination of the two gases thus experimented upon over mercury, producing water exactly as by inflaming the mixture

with the electric spark. One part of spongy platinum is mixed with four of clay, and the whole is rolled into a ball. A platinum wire is fixed into this ball which may be tied to a fine annealed iron wire. The ball, is then slightly ignited, and introduced through the mercury into the mixture. The combination of the oxygen and hydrogen gases is then slowly effected, provided a suitable quantity of clay has been added. As soon as the volume of the gases no longer diminishes, the ball is withdrawn from the mixture by means of the wire, and the volume of the remaining gas is determined. The rest of the process is the same as was described above.

The use of spongy platinum has this great advantage, that it dispenses with the use of a glass tube in which wires have been cemented or soldered by fusion. The results obtained, however, are not so accurate as the inflammation by means of the electric spark; wherefore spongy platinum should never be used in experiments which require extreme precision. When, on the contrary, the quantity of one of the gases so much exceeds the other in the gaseous mixture, that it cannot be inflamed by the electric spark, these balls of platinum are very advantageous, only in that case they must contain more platinum and less clay. According to Turner, the combination of the two gases may still be effected in this manner, even when one of the gases is to the other in the ratio of 1 to 100. Yet, in such a case, tubes of a larger diameter should be used, because in those which are narrow, the experiment proceeds much more slowly.

In these experiments, and in general in all quantitative analyses of gases, it is absolutely necessary, especially if operating upon considerable quantities, to pay a special attention to these points, which are overlooked in the quantitative analysis of solid bodies, namely, the temperature, pressure, and moisture of the gases. When these precautions are neglected, the weight of a gas cannot be induced from its volume, nor can the volumes of the gases measured at different periods be compared together. The omission of only one of these precautions may completely vitiate the results obtained.

PRECAUTIONS RESPECTING THE TEMPERATURE ON EXPERIMENTS  
UPON GASES.

The temperature of the gases is the point which requires the most attentive care. In general it is measured by means of a thermometer suspended near the vessel containing the gas, yet the operator cannot be certain that the temperature is accurately indicated by the thermometer unless he is sure that the gas inclosed in the vessel and the surrounding air have the same temperature. Before measuring the gas this equality of temperature must first be ascertained. If, for example, a mixture of oxygen and of hydrogen gas have to be exploded, the operator before measuring the remaining gas must wait until the temperature has fallen down again to that of the room. When it happens, which is sometimes the case, that the temperature of the room is not the same as before the detonation, when the volume of the mixture was measured, it is necessary, in order to compare with accuracy the volume of the mixture with that of the residuum to reduce them both to the same temperature, and the best for the purpose is to bring them to the zero of the centigrade scale.

\* The most exact method of effecting this reduction is by referring to the following table, based upon the new determination of Rudberg, according to which dry atmospheric air, or any other gas, dilates or increases in volume from the melting point of ice to that of boiling water, in the ratio of 1000 to 1365.

The second and sixth columns indicate the volumes which a gaseous mixture occupies at the various degrees of the centigrade scale, supposing its volume = 1 at zero; the third and seventh columns indicate the logarithms of their volumes; lastly, the fourth and eighth columns show the difference of these logarithms, in order to be able to find readily the logarithms for the fractions of degrees.

\* The calculation may be executed with or without the logarithms. The example given after the table, next page, shows how to operate when the logarithms are not made use of:—

Temperature in Centigrade Degrees.	Volume of Gas.	Logarithm of Gaseous Volume.	Difference.	Temperature in Centigrade Degrees.	Volume of Gas.	Logarithm of Gaseous Volume.	Difference.
0°	1·00000	0·00000	—	15°	1·05475	0·02315	151
1	1·00365	0·00158	158	16	1·05840	0·02465	150
2	1·00730	0·00316	158	17	1·06205	0·02615	150
3	1·01095	0·00473	157	18	1·06570	0·02764	149
4	1·01460	0·00629	156	19	1·06935	0·02912	148
5	1·01825	0·00785	156	20	1·07300	0·03060	148
6	1·02190	0·00941	156	21	1·07665	0·03207	147
7	1·02555	0·01096	155	22	1·08030	0·03354	147
8	1·02920	0·01250	154	23	1·08395	0·03501	147
9	1·03285	0·01404	154	24	1·08760	0·03647	146
10	1·03650	0·01557	153	25	1·09125	0·03792	145
11	1·04015	0·01710	153	26	1·09490	0·03937	145
12	1·04380	0·01862	152	27	1·09855	0·04082	145
13	1·04745	0·02013	151	28	1·10220	0·04226	144
14	1·05110	0·02164	151	29	1·10585	0·04370	144

\* Let us suppose that, before being exploded, the mixture was 145 cubic centimetres, at the temperature of 10° centigrades, and that, after explosion, the residuum has been 63 cubic centimetres, at the temperature of 16° centigrades, and that the operator wishes to know how many hundredths of volumes of the original mixture the residuum occupies. It is easily perceived from the table, that a gaseous mixture which, at 10° occupies a volume of 1·03650, occupies only 1·00000 at 0°. In order to find the volume ( $x$ ) which 145 cubic centimetres measured at 10° would occupy at zero degree, the following proportion is established :—

$$1·03650 : 1·00000 :: 145 : x.$$

Which gives for  $x$ , that is to say, for the volume at zero, 139·89 cubic centimetres. The table indicates also that the volume 1·05840 at 16° centigrades is equal to the volume 1·00000 at zero. The volume  $y$ , which is that which 63 centimetres, measured at 16° centigrades, would have at zero, is found by the following proportion :—

$$1·05840 : 1·00000 :: 63 : y = 59·524.$$



The proportion between  $x$  and  $y$  is therefore—

$$= 139.89 : 59.524 = 100 : 42.55.$$

\* As all gases dilate by heat, according to the same law, the ratio above indicated remains unaltered by the temperature. Consequently, if the operator wishes only to know the ratio, he need not reduce the two gases at zero; it is sufficient to reduce one to the temperature of the other. In the example quoted before, the 63 cubic centimetres, measured at  $16^{\circ}$ , may be reduced at  $10^{\circ}$ , that is to say, at the temperature of the 145 cubic centimetres. The table shows that the weight remaining the same, the volume 1.05840 at  $16^{\circ}$  is equal to the volume 1.03650 at  $10^{\circ}$ , which gives the proportion  $1.05840 : 1.03650 :: 63 : z$ , and the operator finds that  $z$ , that is to say, the volume which 63 cubic centimetres, measured at  $16^{\circ}$  centigrade, would occupy at  $10^{\circ} = 61.7$  cubic centimetres. But  $145 : 61.7$  is the equivalent of the preceding proportion,  $139.89 : 59.524 = 100 : 42.55$ .

If one of the gases had a temperature below zero, for example,  $-5^{\circ}$ , and it was desired to know its volume at zero, the measured volume should be divided by  $1.00000 - 5 \times 0.00365$ , that is to say, by 0.98175.

\* The calculation by means of the logarithms is much more easy, because the operator has only to add or to subtract, whilst in the other method it is necessary to multiply or to divide; wherefore, in the preceding table we have added the logarithms of the numbers which express the volume of gases.

\* The calculation adapted to the above quoted example is as follows:—

\* In order to reduce the 145 cubic centimetres from  $10^{\circ}$  centigrade to  $0^{\circ}$  centigrade, the proportion is as we said,  $1.0365 : 1.0000 :: 145 : x$ . Take, therefore, the logarithm of the number 145 on a table of logarithms with five figures, which is sufficiently exact for all chemical calculations, the logarithm of 1.00000 should be added, but as it is zero, the addition is not made; the operator has, therefore, to subtract from the logarithmic number of 145 that of 1.0365 found in the preceding table, which

produces the logarithm of  $x$ . This number must be looked for in the table of logarithms in which the number corresponding thereto is found. The calculation is, therefore,

$$\begin{array}{r} \text{Log. } 145 = 2.16137 \\ \text{Log. } 1.0365 = 0.01557 \\ \hline \text{Log. } x = 2.14580 ; x = 139.89. \end{array}$$

\* In order to reduce the 63 cubic centimetres from  $16^\circ$  to zero, the proportion  $1.05840 : 1.00000 :: 63 : y$ , gives the following logarithmic calculation:—

$$\begin{array}{r} \text{Log. } 63 = 1.79934 \\ \text{Log. } 1.0584 = 0.02465 \\ \hline \text{Log. } y = 1.77469 ; y = 59.524. \end{array}$$

\* Or else, by reducing immediately the 63 cubic centimetres from  $16^\circ$  cent. to  $10^\circ$  centig., the proportion  $1.05840 : 1.03650 :: 63 : z$ , gives the following logarithmic calculation:—

$$\begin{array}{r} \text{Log. } 63 = 1.79934 \\ \text{Log. } 1.0365 = 0.01557 \\ \hline \phantom{\text{Log. }} 1.81491 \\ \text{Log. } 1.0584 = 0.02465 \\ \hline \text{Log. } z = 1.79026 ; z = 617. \end{array}$$

\* When the residuum has been reduced to the same temperature as the original gaseous mixture, in order to express it into hundredths of the latter, the operator makes the following proportion  $x : y :: 100 : w$ , this latter letter  $w$  expressing the hundredths sought for. The logarithmic calculation is, therefore,

$$\begin{array}{r} \text{Log. } 100 = 2.00000 \\ \text{Log. } y = 1.77469 \\ \hline \phantom{\text{Log. }} 3.77469 \\ \text{Log. } x = 2.14580 \\ \hline \text{Log. } w = 1.62889 ; \text{ therefore } w = 42.55. \end{array}$$

The same value of  $w$  is found by the proportion  $145 : 61.7 :: 100 : w$ :—

$$\begin{array}{r} \text{Log. } 100 = 2.00000 \\ \text{Log. } 61.7 = 1.79026 \\ \hline \phantom{\text{Log. }} 3.79026 \\ \text{Log. } 145 = 2.16137 \\ \hline \text{Log. } w = 1.62889 ; \text{ therefore } w = 42.55. \end{array}$$

\* When the temperature is not expressed in whole numbers, the logarithms of the corresponding volumes of gases must first be calculated. This is easily done by means of the column which expresses the differences. Let us suppose, for example, the temperature to be  $10.3^{\circ}$ , it may be seen that the logarithmic difference between  $10^{\circ}$  and  $11^{\circ}$  is 153; the third of this difference is 46, which number must be added to the logarithm of 1.03650, which gives 0.01603 as the logarithm of the gas at  $10.3^{\circ}$  centigrade.

\* The temperature below zero occurs seldom in experiments. Should this case occur, the operator should first calculate the volume of the gas, and then look in a table of logarithms for the logarithm corresponding to the number expressing this volume.

\* The fraction 0.00365, which expresses the increase of one volume of gas for each degree of the centigrade scale, applies to all gases, either quite dry or quite moist, but it is too small for the gases, apparently dry, which are contained in a vessel which is not completely desiccated by chloride of calcium, because the inside of such a vessel is always coated with an invisible layer of hygroscopic water, which, at a higher temperature, volatilises and augments the volume of the gas. For such cases the former number of Gay Lussac, 0.00375 is more exact.

#### PRECAUTIONS RESPECTING THE PRESSURE IN EXPERIMENTS UPON GASES.

\* The second point to be attended to in accurate experiments upon gases is the pressure. According to Mariotte's law, the volumes occupied by a gaseous mixture at a same temperature, but under various pressures, are inversely as these pressures. It is, therefore, easy to make the necessary correction for the measured volume. We must, however, make two distinctions here; namely, either the liquid which incloses the gas is at the

same height outside and inside of the tube or bell, or else it is higher inside than outside. The latter is the case when the original volume of the gas has diminished by combustion or absorption, and the trough is not deep enough to permit the tube to be sunk sufficiently so as to bring the liquid at an even height inside and outside.

\* In the first case, that is to say, when the liquid (ordinarily mercury) which incloses the gas, has the same height inside and outside, the inclosed gas bears exactly the same pressure as the surrounding air, which pressure is indicated in a direct manner by the barometer. In such an experiment as that related before of exploding the mixture, and in which the operator is obliged to measure the gas a second time after some time has elapsed, if it is observed that the height of the barometer has changed during that time, the corresponding volumes of the gas behave precisely as the barometric height, but in an inverse ratio during the first and the second measuring, provided only, as was said before, that the mercury be at both epochs internally and externally level. Let us suppose that at the moment of measuring the original mixture of oxygen and of hydrogen the barometer stands at 760 millimetres, and that afterwards, on measuring the gas which remains after exploding the mixture, the barometer stands at 750 millimetres, the measured volume of this residuum is to what this volume would be if the state of the barometer had not changed :: 760 : 750. The operator must, therefore, multiply the measured volume by 750, and divide by 760.

\* We are supposing here that the temperature of the gas has undergone no change; and it is also necessary that the states of the barometer of which we have been speaking be reduced to a same temperature, for it is clear, for other reasons, that the pressure of the atmosphere cannot bear a direct proportion to the various heights of the column of mercury in the barometer, except the metal has the same temperature. But as in reality this invariableness of temperature cannot be

arrived at, the thermometer is always fixed close to the column of mercury in the barometer, which indicates, at least very nearly, the temperature of the metal, and from which the above correction may be effected by means of the known coefficient of the expansion of the mercury ( $\frac{1}{5556}$  for each degree cent. of the thermometer), or more conveniently by means of the tables which have been constructed for the purpose.

\* In the second case, when the liquid which incloses the gas is higher internally than externally, the inclosed gas does not bear all the pressure of the atmosphere, that which it bears being less by that which a column of liquid of a height equal to the difference between the outside level and the inside level would exercise. If this liquid is mercury, the pressure of the inclosed gas may be obtained by deducting the difference just mentioned from the barometric height observed at the time. But if the liquid is not mercury the difference of height of the two levels must be multiplied by the specific gravity of the liquid, and divided by the specific gravity of mercury before deducting that difference of barometric height, in order to obtain the pressure of the inclosed gas. The rationale of this calculation is that the pressure exercised on their basis by columns of a same height, but of different liquids, are inversely as the specific gravity of these liquids.

\* It often happens not only that the mercury, which is the substance generally employed to collect gases, stands higher inside than outside, but that above the mercury inside, a liquid is floating which has been employed for absorbing one of the inclosed gases, in which case both calculations must be used. Let us suppose that the barometer stands at 762 millimetres, that the mercury stands in the interior of the tube or bell four millimetres higher than outside, and that a layer of caustic potash of the specific gravity, 1.36 and 10 millimetres thick, is floating over the mercury inside. As the specific gravity of mercury is 13.6, the pressure of the layer of potash-

water is equal to that of a layer of mercury  $10 \frac{1}{3} \frac{2}{3}$  millimetre high, that is to say, one millimetre high, and the pressure of the gaseous mixtures in the tube will accordingly be  $762 - 4 - 1 = 757$  millimetres.

\* Rigorously speaking, it would be still necessary to reduce the difference of height between the two levels of the mercury to a temperature equal to that of the mercury in the barometer: and also the specific gravity of the mercury and that of the liquid which floats on it, should be determined at the same temperature, but these corrections may be neglected, provided the difference of the two levels of the mercury and the height of the supernatant liquid above the metal are not very considerable. In general the influence of the changes of the barometer is inconsiderable, and a difference of about half a millimetre does not interfere.

\* If the internal level of the mercury were lower than that outside, the tube containing the gas should be raised until the internal level has become equal to, or more than that outside.

\* In delicate experiments, and especially when the weight of gas has to be deduced from its volume, the pressure of the gas is generally reduced to a barometric height of 760 millimetres; not that it is absolutely necessary to do it, but because the weights of gases are rigorously estimated at that barometric height, and also because the mean pressure of the air in places which are not considerably above the level of the sea, nearly balances a column of mercury 760 millimetres high. If the volumes of gases have to be compared only, they may be reduced to any barometric state, provided it be uniformly employed for all the volumes.

PRECAUTIONS TO BE OBSERVED RESPECTING THE MOISTURE IN  
EXPERIMENTS UPON GASES.

\* The third point which deserves attention, is the moisture with which gases are impregnated. When atmospheric air is

exploded with hydrogen, for the purpose of determining the quantity of oxygen which it contains, the third part of the volume of the gas which has disappeared by explosion, cannot be looked upon as oxygen, because part of the water formed is in the state of vapour, which thus increases the volume of the gaseous mixture. When a portion of a dry gaseous mixture is absorbed by an aqueous liquid, that which thus disappears does not, for the same reason, represent the volume of the gas absorbed, for the aqueous vapour which has disengaged from the liquid must be taken into account. In the same manner, the weight of a moist gas, or of a gas collected over water, cannot be ascertained from its volume, except the aqueous vapour which it contains is taken into account, because the tables which have been published on the weight of determined volumes of gases, assume that they are in a perfectly dry state.

\* But the space occupied by permanent gases is completely, or incompletely saturated, by aqueous vapour; the first case occurs always when there is an excess of water, or of aqueous liquid.

\* When, at the temperature which the gas has, the space which it occupies is completely saturated with aqueous vapour, the amount of pressure which this vapour, by virtue of its tension, contributes to the total pressure experienced by the moist gas, or gaseous moisture, is easily found, and the pressure of the gas, or of the dry gaseous mixture, is also very easily calculated, as also that which it would occupy under any determined pressure. In effect, it is a law well corroborated by experience, that the vapour of water, or of any other liquid whatever, can, at each temperature, acquire only a certain maximum of tension dependent on that temperature, and that this maximum of tension is always attained when there is excess of liquid, whether the space in which it is spread is free or occupied by one or several gases. The pressure which a gas saturated with moisture exercises is, therefore, of a double kind, namely, the pressure of the dry gas, and that of the aqueous vapour. The following table, constructed by Biot, indicates the

latter pressure, that is, the tension of aqueous vapour for the temperatures which occur in experiments on gases.

Temperature in centigrade degrees.	Tension in millimetres.	Temperature in centigrade degrees.	Tension in millimetres.	Temperature in centigrade degrees.	Tension in millimetres.
— 11	2.46	+ 3	6.12	+ 17	14.47
— 10	2.63	+ 4	6.52	+ 18	15.35
— 9	2.81	+ 5	6.95	+ 19	16.29
— 8	3.01	+ 6	7.40	+ 20	17.31
— 7	3.21	+ 7	7.87	+ 21	18.32
— 6	3.43	+ 8	8.38	+ 22	19.42
— 5	3.66	+ 9	8.91	+ 23	20.58
— 4	3.91	+ 10	9.48	+ 24	21.81
— 3	4.17	+ 11	10.07	+ 25	23.09
— 2	4.45	+ 12	10.71	+ 26	24.45
— 1	4.75	+ 13	11.38	+ 27	25.88
0	5.06	+ 14	12.09	+ 28	27.39
+ 1	5.39	+ 15	12.84	+ 29	29.05
+ 2	5.75	+ 16	13.63	+ 30	30.64

\* When by the method which has been indicated before, the operator has determined the pressure of the moist gas or gaseous mixture, and has taken care at the same time to examine its temperature, he has only to take in the above table the tension of the aqueous vapour corresponding to the temperature, to obtain the pressure of the dry gas or gaseous mixture. Let us suppose, for example, that after having deducted the difference of height between the two levels of the mercury, and made the correction necessitated by the layer of water floating over the mercury inside, the pressure is 75 millimetres, and the temperature of the gas is  $+ 11^{\circ}$  cent., the table indicates that 10.07 millimetres must be deducted for the aqueous vapour, and consequently the pressure borne by the dry gas is 746.93 millimetres.

If the aqueous liquor floating over the mercury inside is not pure water, if, for example, it is a saline solution, the above table cannot, rigorously speaking, be employed, because aqueous



vapour, when in contact with a saline solution, possesses, at each degree of temperature, a maximum of tension, which is less than when it is in contact with pure water. If, therefore, in such a case, it was desired to effect, with all the required precision, the correction referring to the aqueous vapour, the operator should determine, by a separate experiment, what is the tension of the vapour of the saline solution employed at the temperature of the gas which is enclosed above the liquor. But if the solution is not very concentrated, the numbers expressing the tension in the preceding table are sufficiently accurate.

\* When the gas or gaseous mixture operated upon is not saturated with aqueous vapour, and is not either before or during the experiment put in contact with an excess of water, Biot's table can no longer be used. The moist gas must then be completely saturated by aqueous vapour, by adding water, and by means of the method which has been indicated, the pressure of the dry gas which it contains may be calculated, or, which is better still, it may be deprived of all its water by introducing into it a small piece of chloride of calcium fixed at the end of an iron wire, and it is left in contact with the gas until it ceases to absorb any thing.

\* In general it is advisable during the analysis, not to put the gases in contact with water or an aqueous liquid, because a more or less considerable quantity of gas is thus absorbed, which cannot easily be determined in an accurate manner.

#### PRECAUTIONS TO BE TAKEN IN REFERENCE TO CAPILLARITY IN EXPERIMENTS UPON GASES.

\* Lastly, a fourth point must also be taken into consideration in experiments upon gases, namely, capillarity. When the level of the mercury has been brought to the same height inside and outside the bell containing the gas, the latter does not as yet bear, rigorously speaking, the pressure of the atmosphere; because when mercury is poured into two vessels of

unequal capacity, open at the top, and communicating together, it stands lower in the smaller vessel than in the larger one, on account of capillarity. The reverse is the case for water, and all liquids which wet glass vessels and form a concave surface. They stand higher in narrow vessels than in large ones, and impart a greater pressure than that of the atmosphere to the gas when their level is equalised inside and out of the tube. The difference, however, and the consequent correction are so trifling, when the diameter of the tube exceeds half an inch, that it may be altogether neglected.

\* The three corrections necessitated by the temperature, pressure, and moisture must, as a rule, be made in all experiments upon gases, though the order in which these corrections are made, matters but little. Yet it is better to begin by that for the pressure, than by that for the aqueous vapour, which, properly speaking, is only a correction of the pressure, and to terminate by that for the temperature.

There is one more circumstance to be taken into account, and which was first pointed out by Faraday. In effect the dry gases, when kept over mercury, are, after a long space of time, replaced by atmospheric air. This phenomenon is probably owing to this, that the contact between the glass and the mercury is not perfect, but that a sufficient space is left between these two bodies to permit the interchange of the gases. Yet this interchange requires a whole year to become complete. The operator should not, therefore, defer the analysis of gases too long when they are kept over mercury.

SEPARATION OF HYDROGEN GAS FROM NITROGEN GAS, AND  
NITROGEN GAS FROM OXYGEN GAS—ANALYSIS OF ATMOSPHERIC AIR.

\* The analysis of a mixture of oxygen gas with nitrogen gas, or of hydrogen gas with nitrogen gas, is performed exactly as was described (page 677).

If the gaseous mixture consists of hydrogen and of nitrogen

gases, its volume is determined, and about half that volume of oxygen gas is added. The volume of the gaseous mixture is then determined again, and the electric spark is passed through. The diminution of the volume easily gives the quantity of hydrogen gas contained in the mixture, and which amounts to the two-thirds of the volume of the gas which has disappeared. Even when the whole of the gas operated upon consists altogether of hydrogen, the quantity of the oxygen gas added will have been sufficient to convert it into water. The gas which remains after the explosion is nitrogen only, plus the excess of oxygen employed. The volume of the nitrogen is determined by deducting the volume of the hydrogen gas from that of the gaseous mixture experimented upon.

When a gaseous mixture consists of oxygen and of nitrogen, as, for example, atmospheric air, the analysis proceeds in the same manner; only, instead of oxygen, hydrogen is the gas added. It is a little more difficult to procure rapidly small quantities of hydrogen than small quantities of oxygen. If it is not necessary that the hydrogen gas added be perfectly free from aqueous vapour, it may be disengaged from a flask containing zinc, and dilute sulphuric acid. The flask in which the zinc is put, and on which water is poured, must be closed airtight with a cork perforated with two holes; one of these holes admits a funnel, which descends almost to the bottom of the flask; from the other a disengagement glass tube issues. It is advisable to use a very small flask. After having poured the sulphuric acid through the funnel, the operator must wait until the hydrogen has expelled all the atmospheric air from the apparatus, and burns quietly upon being set fire to. But the disengagement of the gas must be very slow, in order that the gas may not carry too much water. The gases employed for this experiment must be pure, and therefore distilled zinc must be used to produce it.

\* The hydrogen produced is admitted into the mixture, until the volume of the latter is doubled. Such a quantity of hydrogen

is sufficient to convert the whole of the gas under examination into water, if it consisted altogether of oxygen, without any nitrogen at all. When, however, the gas to be analysed is atmospheric air, which contains nearly four volumes of nitrogen for one of oxygen, hydrogen is added in the proportion of only half the volume of the gaseous mixture. After having accurately measured the volume of the gas which has been added, an electric spark is passed through the mixture. If the volume has diminished one-third, it indicates, as usual, the volume of the oxygen gas contained in the gaseous mixture experimented upon. The quantity of the oxygen gas gives that of the nitrogen. If the mixture of oxygen and of nitrogen represented fifteen volumes, and if after having added seven volumes of hydrogen, the combustion, by means of the electric spark, has caused nine of these twenty-two volumes to disappear, the fifteen volumes contained three volumes of oxygen gas, and twelve of nitrogen.

\* It is scarcely necessary on analysing atmospheric air, to make the correction for the moisture of the gas measured after the explosion, because the air experimented upon is not perfectly dry, and the hydrogen gas added thereto is ordinarily moist.

\* We have already said (page 680) that for the analysis of atmospheric air, the operator may use a glass tube perforated at the open extremity, with a hole capable of being closed by a glass stopper.

If the gaseous mixture consists of oxygen, hydrogen, and nitrogen, a portion thereof is exploded by means of the electric spark, without adding anything to it. After the explosion, the nitrogen remains mixed either with oxygen gas, or with hydrogen gas. Oxygen is then added, in order to see whether the electric spark, being passed through the mixture, will again cause a diminution of volume. If this takes place, it is a proof that after the first explosion, nitrogen and hydrogen remained, and the composition of the gaseous mixture may then be easily

determined. But, if no diminution of volume ensues, the gaseous residuum after the explosion is a mixture of nitrogen and of oxygen. Hydrogen is then introduced in it, and the mixture is exploded; from the quantity of oxygen, calculated from the diminution of volume, that of this gas which had been added before, must be deducted.

Several other methods have been proposed for the analysis of these gaseous mixtures, and especially for that of atmospheric air, but they do not yield results so accurate as that which has been described, and they need not, therefore, be related here. The methods most usually employed, which consist in absorbing the oxygen, are those by means of phosphorus, nitric oxide, and sulphuret of potassium.

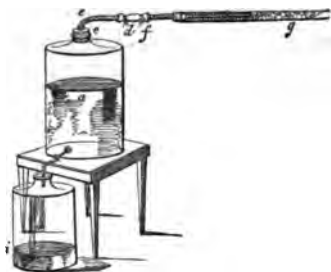
\* One of the best methods of analysing atmospheric air, after that which consists in determining the quantity of oxygen, by deflagrating it with hydrogen gas, appears to be that which was proposed by Brunner. According to this process, in order to find the quantity of oxygen, a determined volume of oxygen is passed over iron in a very fine powder, which becomes thus oxidised, and the weight of which increases in proportion as the air employed contains more oxygen. The iron is prepared by reducing peroxyde of iron by hydrogen gas. The experiment is executed in an apparatus similar to that which Brunner employs for determining the water contained in the atmospheric air, and which will be shown presently.

\* Another method by which the quantity of oxygen contained in the atmospheric air can be determined with great accuracy, was proposed by Theodore Saussure. It consists in treating a known but considerable volume of air, by moist granulated lead, which is kept in constant agitation; the lead absorbs completely the oxygen, and also the carbonic acid, leaving the nitrogen in a pure state. Gay Lussac absorbs the oxygen by copper moistened with sulphuric or muriatic acid.

\* Besides nitrogen and oxygen, the atmospheric air contain very small quantities of carbonic acid and aqueous vapour. Several instruments, called hygrometers, have been contrived for estimating the quantity of the latter, but which indicate only in an indirect manner the proportion of water contained in the air.

\* Brunner employs a very simple apparatus for determining immediately the quantity of water contained in the atmospheric air.

A cylindrical bottle *a*, provided with a tap, is filled with water. A glass tube *d, e*, bent at right angle, is hermetically fitted to it at *c*, the horizontal branch of which contains a few small pieces of chloride of calcium, which are kept in place by some loose cotton wadding put at *d* and *e*. At the extremity *d*, a tube, *g, f*, is connected by a tube of indian rubber, which tube, *g, f*, contains a hygroscopic substance. Brunner employs for the purpose as much fine asbestos as is sufficient to fill up the tube,



without impeding the passage of the air. The asbestos is then moistened as uniformly as possible with ordinary sulphuric acid (English). According to Brunner, asbestos moistened with sulphuric acid is preferable to chloride of calcium. The tube must be accurately weighed before the experiment.

\* Every thing being ready, the tap is opened, and the water of the bottle *a*, is allowed to flow, and is received in another flask, *i*, in which it can be measured. The water is replaced by an equal bulk of atmospheric air, which has passed through the tube *g, f*, in which the water which it contained will have been

absorbed by the sulphuric acid. In order that the water may be absorbed as completely as possible, the flow of the water from the bottle must be regulated in such a manner, that it does not run too rapidly, for otherwise a portion of the water contained in the air might escape absorption.

\* Brunner has since made some improvements to his apparatus, to which he gave the name of *Aspirator*.

\* If, after the water has run off, the tube *g, f*, is weighed, the increase of weight will indicate the quantity of water contained in a given quantity of air. The pieces of chloride of calcium were introduced in the tube *d, e*, for the purpose of preventing a very small quantity of aqueous vapour of the water in the bottle from finding its way to the sulphuric acid tube, the weight of which would thus be augmented.

\* Saussure employs, for measuring the carbonic acid of the air, a globular receiver of a known capacity, having a narrow opening, capable of being corked up air-tight. This receiver is first emptied by means of an air-pump, and the air to be analysed is introduced into it; baryta water is then poured in, it is corked up, well shaken, and left at rest for a long time, yet the baryta-water must not be left in contact with the air more than a few days, because, besides carbonate of baryta, crystals of peroxyde of barium would be formed. The carbonate of baryta which has been produced is removed by two operations.<sup>1</sup> In the first, the baryta-water is withdrawn with the precipitate floating in it, it is left at rest, and the clear liquor is poured off; the precipitate is washed and then dissolved in muriatic acid. The second operation consists in pouring muriatic acid in the receiver, in order to dissolve the carbonate of baryta which adheres to its sides. The two muriatic acid liquors are then mixed together, and the baryta is precipitated therefrom by muriatic acid. From the quantity of sulphate of baryta obtained, that of the carbonic acid which existed in the carbonate of baryta is calculated.

\* A method similar to that employed by Brunner for the

determination of the water contained in the atmospheric air would probably answer equally well for the determination of carbonic acid contained in the air. To the bottle, *a*, which is full of water, a tube similar to that spoken of (page 698,) is fixed, but which must be three feet or three feet and a half long by about a quarter or three-eighths of an inch large. The part of the tube towards the bottle, and which is one foot long, is filled with asbestos moistened with sulphuric acid. The rest contains hydrate of lime, which is separated from the asbestos by cotton wadding. The tube communicates with another tube filled with asbestos and sulphuric acid, and which was weighed separately.

\* After the air, the volume of which is determined from the quantity of water which has run off, has deposited its moisture in the tube of which I have just been speaking, it also parts with its carbonic acid, which is taken up by the lime through which it passes. But as it is then in a state of perfect dryness, and consequently capable of absorbing water, the latter must again be completely removed by the last portion of the tube which is filled with asbestos and sulphuric acid. This being done, it is clear that this increase of weight of the long tube which is filled partly with asbestos and sulphuric acid, and partly with hydrate of lime, indicates the weight of the carbonic acid of the air. The quantity of water which the latter contains is determined in the same manner by the increase of weight of the tube which contains the asbestos and sulphuric acid only.

\* In these experiments care must be taken that the lime employed is well calcined. It is first moistened with a little water, and when perfectly slaked, a little water is again poured upon it, so that it forms small curdy lumps upon being stirred. This is the proper state of moisture it should have, and which the operator should endeavour to attain. If the lime is too dry, its absorbent power is not strong enough; if too damp, it becomes difficult to make it penetrate the bent part of the tube.

\* The volume of the air under examination must not be too small, because the increase of weight of the lime would be too inconsiderable.

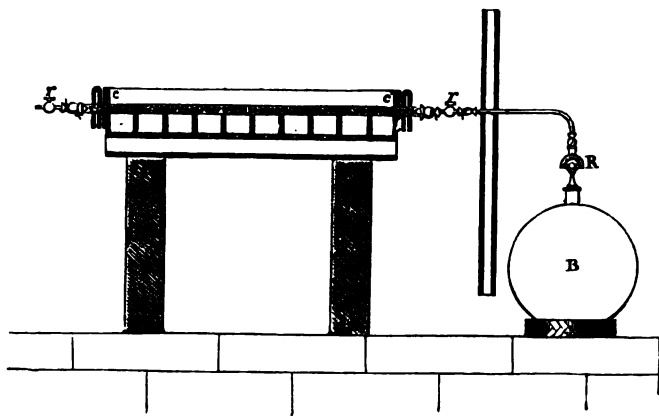


The following note is by E. Peligot :—

\* [Important researches have of late been undertaken with a view to determine with accuracy the composition of the atmospheric air.

\* The analysis of gaseous mixtures by volumes, obliges the analyst to operate upon small quantities of gas, and is subordinate to the graduation of apparatuses, the accuracy of which cannot be controlled except with great difficulty. This method of analysis always requires that the volume of the gas should be determined, which is difficult, and also its temperature and pressure, either in the dry state or saturated with aqueous vapour, all of which circumstances render the analysis by weight, when possible, much preferable, because the analysis may then be performed upon a gaseous mass much more considerable, and by means of apparatuses, the accuracy of which may at all times be verified, if not in an absolute, which is generally of no moment, at least in a relative manner.

\* MM. Dumas and Boussingault have determined the proportion of the oxygen and of the nitrogen in the air, by weighing each of these two gases produced by considerable quantities of atmospheric air. Their apparatus is here represented :—



\* This apparatus consists,

1st, Of a glass receiver B, of about 15 litres capacity, and which may be emptied by means of the air-pump :

\* 2nd, Of a tube *cc*, in hard glass, and filled with metall copper obtained from the reduction of protoxyde of copper b means of hydrogen gas, and to which tube, cocks *rr*, are adjusted, by means of which a vacuum may be produced in the tube also. The weight of both the glass-receiver and the tube has been accurately ascertained :

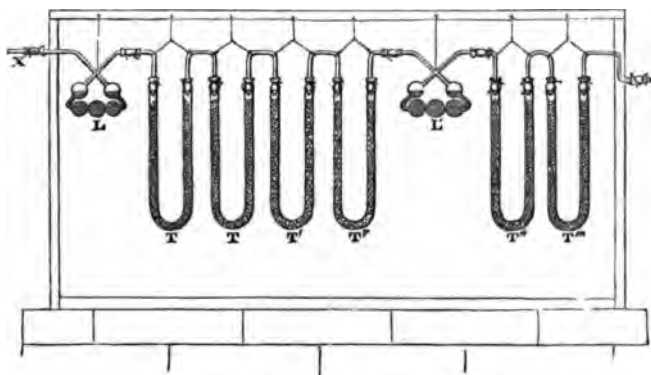
\* 3rd, In a series of tubes through which the air must pass before coming in contact with the copper ; these tubes are eight in number, suspended to a wooden frame, and connected with the first part of the apparatus by means of the cock *r*, and a tube of caoutchouc. These tubes contain different substances for purifying and desiccating the air submitted to analysis.

\* The *modus operandi* is as follows:—The glass receiver *F* and the tube *cc*, are accurately weighed, after having been exhausted with the air-pump, in the balance called *balance de Fortin*, the different parts of the apparatus are then connected by means of Indian rubber tubes, the copper is brought to a red heat, and the operator carefully opens the first cock *r*, which permits the air to enter the tube *cc*, the copper immediately takes up the oxygen of the air. A few minutes afterwards the second cock *r*, and that of the glass receiver *R* are opened, and the nitrogen gas penetrates then into the exhausted receiver *B*. The cocks being kept open, the air is aspirated, and after having previously been deprived of its water and carbonic acid, it reaches the copper tube, where it parts with its oxygen, so that only pure nitrogen passes into the glass receiver. When it is full, or nearly so, all the cocks are closed, the glass receiver and the tube *R*, which are full of nitrogen, are then separately weighed, and then weighed a second time after having again exhausted them. The difference of weight indicates that of the nitrogen. That of the oxygen is found by the increase of weight which the tube which contains the copper has acquired during the experiment.

\* The series of tubes which are employed for purifying the air, are as follows :—

1st. *L* is a Liebig's apparatus, containing a concentrated

solution of caustic potash, connected by means of a tube of caoutchouc to the glass tube X, which opens in the air of the room in which the experiment is made, or which is connected to the receivers or gasometers filled with the air to be analysed.



2nd. TT are two tubes filled with pumice-stone in small pieces, moistened by a solution of potash.

3rd. T'T'' are two other tubes, the first (T') contains ordinary potash in pieces, the second (T'') pieces of potash previously ignited. The object of these tubes is to deprive the air completely of its carbonic acid; the latter absorbs besides the greatest portion of the water which it contains, or which it has absorbed from the preceding parts of the apparatus.

4th. L' is a Liebig's apparatus, containing sulphuric acid, recently boiled.

5th T''' T''' are two tubes filled with pumice-stone, moistened with the same sulphuric acid as above.

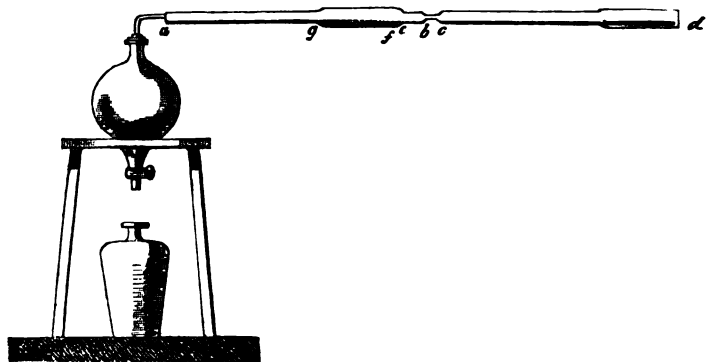
In the three tubes the air becomes completely dry. The pumice-stone, moistened with sulphuric acid, employed for sitting and drying gases, should first be moistened with sulphuric acid, and then ignited, before using it, for it otherwise disengages sometimes a little muriatic acid on moistening it with sulphuric acid, which would cause a great perturbation in the analysis.

\* The weighing of the receiver and of the tube, when full of

nitrogen and when exhausted, requires besides peculiar dispositions of the balance, for which the reader is referred to the *Mémoire* of MM. Dumas and Boussingault, (*Annales de Chimie et de Physique*, 3<sup>ème</sup> Série, tome 3).

\* Before MM. Dumas and Boussingault, Brunner had endeavoured to determine the weight of the oxygen contained in atmospheric air, by absorbing that gas with phosphorus. The apparatus which he employed is represented here.

\* *a b* is the eudiometer-tube; *c d* is the tube for fixing the carbonic acid and water of the aspirated air. The eudiometer tube is prepared as follows:—A piece of phosphorus, weighing about one gramme, is introduced into the part *b e*, and by turning the tube on its axis, the operator endeavours to make the melted phosphorus adhere to the sides; the swelled part *c*



the tube *f g* is loosely filled with carded cotton wool, which however, must not extend beyond *f*, so that there is an empty space of about one inch between *f* and *e*.

\* This tube, thus filled, is adapted to the Aspirator and to the tube *c d*, by means of metallic collars, cemented with sealing wax. The Aspirator is filled with olive oil, which M. Brunne prefers to water, thus avoiding the absorption of a small quantity of nitrogen, and also the tension of aqueous vapour, which would modify the volume of the gas, and would render a correction necessary.

\* Before beginning the experiment, the phosphorus at *e* and *f* is first fused, whilst the oil is allowed to flow off. The phosphorus soon begins to burn, and the product of the combustion passes into the tube filled with cotton. This product is a mixture of phosphorous acid with a little oxyde of phosphorus. When three or four ounces of oil have flowed off, the experiment is suspended by shutting the cock of the aspirator ; the apparatus is allowed to cool, and the tube *a b* is carefully weighed.

\* The object of this preliminary experiment is to form a little phosphorous acid, which, having a great affinity for oxygen, serves, during the eudiometric experiment, to absorb the small residuum of oxygen which might have escaped the action of the phosphorus.

\* In order to perform the eudiometric part of the experiment, the tube *a b*, which has been weighed, is re-adjusted, the phosphorus is gently heated, so as to fuse it, and the cock of the aspirator is then opened, in order that the oil may flow ; it is collected in a vessel graduated with much care. M. Brunner employs one hour for the running off of 1731 cub. centim. of oil. The dimensions of the tube which suit this quantity are—length of *a g*  $5\frac{1}{2}$  inches ; of *g f*  $4\frac{1}{2}$  inches ; internal diameter of *a g*  $\frac{1}{16}$ , of *g f*  $\frac{1}{8}$  of an inch.

\* The combustion of the phosphorus once begun, continues without intermittence and very uniformly, without applying heat externally, with the ordinary light which phosphorus emits in the dark. The light should not be bright, producing phosphoric acid, the effect would be too rapid, and a great portion of the product would pass into the aspirator.

\* The experiment being finished, the tube *a b* is again weighed, and the increase of weight gives the quantity of oxygen which has been fixed. The weight is converted into volume by calculation, and it is compared with that of the nitrogen, which is represented by that of the oil which has run.

\* The tube *c d*, for fixing the carbonic acid and water of the atmospheric air, contains slaked lime and asbestos moistened with concentrated sulphuric acid.

\* This method is assuredly preferable to that which M. Brunner

had first proposed, and which was alluded to by H. Rose ; it is also preferable to all the other methods of determining the composition of the air by volume ; but it is attended with difficulties of execution, and liable to inaccuracies, which are avoided by that employed by MM. Dumas and Boussingault. Thus, besides the difficulty of weighing straight tubes of a somewhat considerable length, it is not always possible to prevent a vivid combustion of the phosphorus, which either breaks the tube, or carries the products of the combustion into the aspirator ; it is even doubtful whether a small quantity of phosphorus must not be volatilised and mechanically carried away by the nitrogen into the aspirator.

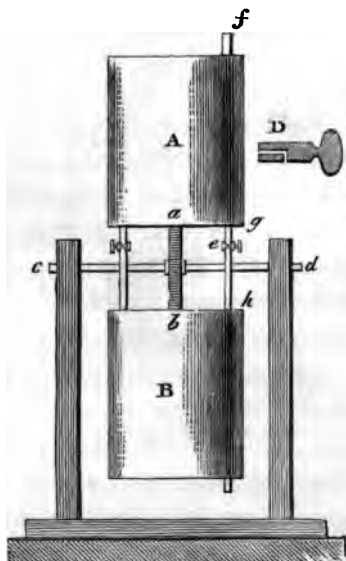
\* The principal defect of this method, however, is the necessity of taking the density of the nitrogen, if it be wished to obtain the composition of the air in weight, and the density of the oxygen, if it be wished to obtain that composition in volumes.

\* MM. Dumas and Boussingault's method does not require any appreciation of volume, because it is independent of all elements foreign to the operation itself, and it has even led these chemists to indicate and to rectify the density of the two principal gases which constitute the atmosphere.

\* M. Brunner applied, also, his aspirator, which he greatly improved, to the dosing of water and carbonic acid. That apparatus is very suitable both for determining accurately the volume of the air, or of the gas operated upon, and for evaporating or drying substances, either in the water or in the oil-bath. It allows also of burning certain bodies in a stream of air. It is represented in the figure following.

\* *A B*, are two cylindrical vessels of tinned or japanned iron, or of copper, of equal capacity, for example, about one cubic foot, closed on both sides, and connected by an iron rod *a b*, on which the apparatus may turn as round an axis, so that the two vessels occupy successively the same place. Suppose the vessel *A* to be full of water, it is evident that on allowing the liquid to run through the cock, *c*, of the tube *g h*, into the lower vessel,

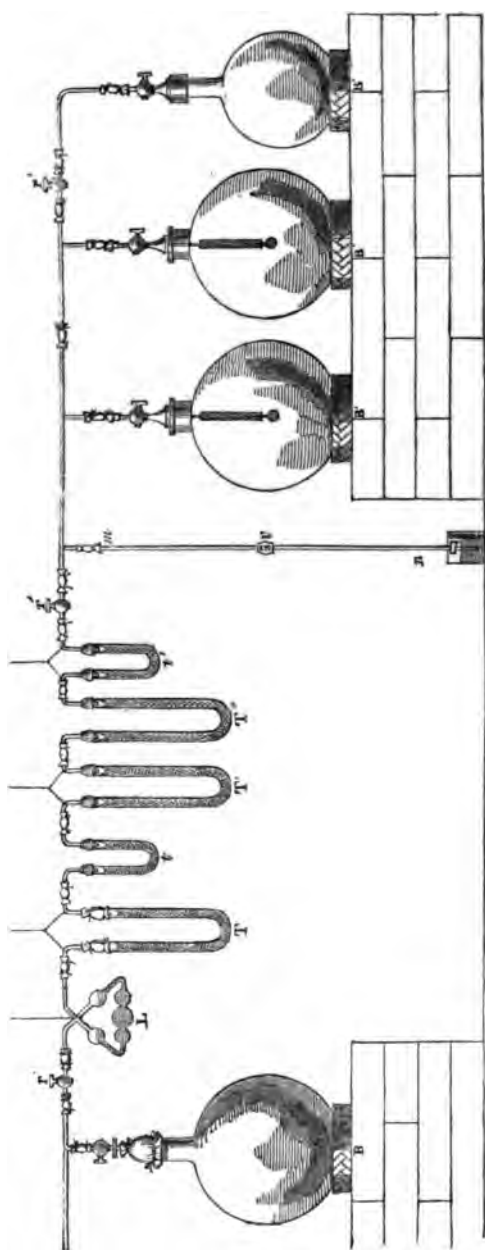
the vessel *A* will become full of air, which enters by the opening *f*. The water having run off from vessel *A* into vessel *B*, the opening is closed, the apparatus is then made to revolve on its



axis and the same operation is repeated, that is to say, the water is made to run from vessel *B* into vessel *A*. In order that the air of the lower vessel may escape, the cock, represented at *D*, is to be opened.

\* The tubes and other apparatuses, through which the air must be passed, are adjusted at the opening *f*.

\* M. Boussingault, and after him M. le Blanc, have turned their attention to the determination of the carbonic acid contained in them. This experiment may now be easily performed by means of the aspirator, or of a graduated apparatus provided with a cock, at the lower extremity, for the discharge of the water, and of a sufficient number of Liebig's apparatuses and of V-shaped tubes, some containing sulphuric acid to exsiccate the air, the others containing potash to absorb the carbonic acid; we shall represent here only the apparatus employed by M. le Blanc, for the estimation of the carbonic acid contained in closed rooms.





\* The receiver *B*, which communicates with another receiver of the same form, is employed, as well as the latter, to collect and keep the air to be analysed. The opening is closed by a piece of caoutchouc, kept in shape internally by a cone made of horn, and a cock is fixed in the narrower portion of the exterior cone of caoutchouc. MM. Dumas and Boussingault have shown by experiment that receivers so prepared, and in which a vacuum has been made, can be used for the purpose of receiving the air of a place far distant, and remain in a perfectly efficient condition.

\* These receivers, at the time of the experiment are connected with two receivers *B' B'* previously exhausted, and which act as aspirators. But the air which flows from *B B* to *B' B'* must pass through the apparatus *L* and *T*, in which all the moisture is absorbed by the sulphuric acid which they contain, and in passing through the tubes *T' T''* it loses all its carbonic acid; the first contains pumice-stone moistened with alkali, the second contains pumice-stone moistened with concentrated sulphuric acid.<sup>1</sup> The weight of the condensed carbonic acid is determined by the increase of weight of these tubes. The small tubes *t* and *t'* are indicators, the weight of which must not alter during the experiment, the first contains sulphuric acid, the second contains potash.

\* The air which has abandoned its carbonic acid to the potash, is estimated in volume, for which reason the receivers *B' B'* should be accurately gauged, and the following dispositions are besides adopted for the purpose of ascertaining, with sufficient accuracy, the temperature of the air of the receivers, and its tension. A very delicate thermometer is placed in the interior of each receiver, the degrees of which, marked upon an ivory rod, are visible through the sides of the glass receivers. Between the receivers and the tube *t'* a vertical glass tube *mn*

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<sup>1</sup> The pumice-stone moistened with sulphuric acid should have been previously calcined in contact with that acid, for it might otherwise disengage under the influence of concentrated sulphuric acid, vapours of muriatic acid, which would vitiate the result.

is suspended and tied by an Indian-rubber tube to the T-shape tube, which is bent downwards.

This tube is graduated into millimetres, and plunges into a mercurial trough. By means of a steel slide (*vernier*) *v* tenths of millimetres can be estimated. When the operator wishes to measure the height of the column of mercury lifted by the aspiration of the exhausted receivers B'B', the surface of the mercury in the trough is brought to the zero of the graduated scale, indicated by the contact of a little cone of ivory fixed to the divided tube. The height of the column of mercury, with the necessary correction for capillarity, being subtracted from the barometric height at the time, gives the tension of the air in the receivers. The operator knowing besides, beforehand, the degree of vacuum of the receivers, before the experiment, possesses all the necessary data for reducing the volume of the collected air, to 0° and 0<sup>m</sup>76, and for calculating the weight, that of a *litre* of dry air being known.

\* The apparatus, represented above, being ready, the operator begins by exhausting the air which it contains by aspirating it by means of an auxiliary receiver B', in which a vacuum has previously been made; the cock *r''* is then shut. Having ascertained that the height of the column of mercury raised up remains uniform for several hours, the cocks of the receivers BB are gradually opened; the air of these receivers spreads uniformly in the apparatus. The cocks of the receivers B' B' are then cautiously opened, and the gas passes into these receivers with a rapidity which is guided by the operator, as he sees the bubbles succeeding each other through the sulphuric acid of Liebig's apparatus. The aspiration having ceased, or nearly so, the cock *r* is to be shut, and the temperature and pressure are allowed to equilibrate. After some time, the cock *r'* is to be shut also, and shortly afterwards, the temperature of the air of the receivers is repeatedly examined. The operator measures also the height of the column of mercury raised up, and in order to be able to weigh the carbonic acid tubes, the operator has nothing more to do than restore dry air to them, which is done

by shutting the cock *r'*, and the air of the room is admitted by opening the cock *r*.

\* Lastly, in order to complete the narrative of the principal methods which have been hitherto adopted for the determination of the constituents of the atmospheric air, we should mention the process by which M. Boussingault has demonstrated in a paper published in 1834, the presence of the very minute proportion of the hydrogenous constituent which it contains, and which the author of the present work, doubtless, unwittingly omitted.

\* In exploding a mixture of pure hydrogen and of atmospheric air, deprived of its carbonic acid, M. T. de Saussure was led to suspect the presence of a combustible gas in the air, for he always obtained, after combustion, a certain quantity of carbonic acid; his experiment indicating nothing respecting the nature of this gas, which may be carbonic oxyde, or a hydrocarburet, M. Boussingault endeavoured to determine its nature, and succeeded in demonstrating in the air the presence of hydrogen, probably in the state of hydrocarburet. In effect, if perfectly dry air is passed over protoxyde of copper, previously brought to a red heat, he invariably obtained a certain quantity of water.

\* His apparatus consists of a tube of hard glass, surrounded by a tinsel foil, and filled with oxydised copper turnings; this tube rests upon a horizontal grate, and is kept at a red heat pending all the duration of the experiment, which usually lasts fifteen or eighteen hours; both extremities of the tube, to which tubes of a smaller diameter are soldered by the enameller's lamp, communicate with two tubes of equal dimensions, and filled with asbestos moistened by concentrated sulphuric acid; one of these tubes is for receiving the water produced by the contact of the dry air with the protoxyde of copper; the other is to ascertain that the air has been entirely deprived of moisture by the exsiccating apparatus which precedes it, and which consists of a tube also filled with asbestos moistened with sulphuric acid, and communicating with another tube three

metres long, and filled with fragments of chloride of calcium so that the air, as it issues from a gasometer, or is aspirated by means of a bottle full of water or of mercury, and which is allowed to flow by a cock placed towards the bottom traverses first the latter tube, and becomes thoroughly dry in passing through the sulphuric acid, the last of which sulphuric acid tube shows this to be the case, because its weight remains unaltered during the experiment; the air lastly comes in contact with the oxydised copper turnings, which decompose the hydrocarbon which it contains, producing water, which is retained by the other sulphuric acid tube which is connected with the combustion-apparatus; by weighing the latter tube before and after the experiment, the weight of the water absorbed gives that of the hydrogen resulting from the air experimented upon.

\* In order that the water so produced may be truly referred only to the combustion of the hydrogenous constituent in the red hot tube, no corks must be employed; caoutchouc must be used everywhere. Moreover, before beginning the experiment, fifteen or twenty *litres* of air must be passed through the combustion-tube, in order to expel the internal moisture of the tube; it is only when this has been done that the apparatus is connected with the sulphuric acid tube in which the water produced by the hydrogenous constituent of the air is to be condensed.

M. Boussingault ascertained that the water collected in this tube was always in much more considerable quantity than that condensed in the other sulphuric acid tube, although the surface presented by both to the air was equal; after several experiments, the weight of the latter was found not to have augmented; and, moreover, in taking at various times during the operation the weight of the sulphuric acid tube for the condensation of the water produced by the hydrogenous constituent of the air, he ascertained that the production of the water was in proportion with the quantity of the air which had traversed the apparatus, whilst, if it had been accidental water, it

would have been condensed in larger proportion at the beginning of the experiment.

\* All these precautions are absolutely necessary to establish the probability of the presence of a hydrogenous constituent in the air, but in so small a proportion that the hydrogen contained in one part of air is, at the maximum, equal to 0.000008 of its weight, or 0.00013 of its volume.<sup>1</sup>

\* It is much to be desired that these examinations be repeated and verified; perhaps it would be well to examine whether sulphuric acid, which condenses several hydrocarbons, should not be replaced by another equally exsiccating substance, for example, by anhydrous phosphoric acid. The estimation of the carbonic acid, which M. T. de Saussure found had been produced after he had deprived the air of that which it contains, should be also attempted.

#### SEPARATION OF HYDROGEN GAS FROM NITROGEN GAS—DETERMINATION OF AMMONIA.

The process for analysing a mixture of nitrogen and of hydrogen has been described before. There remains only

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<sup>1</sup> Several chemists are of opinion that this hydrogenous and carbonaceous constituent may be the gas of marshes, ( $\text{CH}_4$ ) considerable quantities of which are constantly disengaging in the air. In addition to this the air occasionally contains substances, the existence of which becomes apparent by the agues, epidemics, and other diseases; which substances, although at times in sufficient quantity to affect the organ of smell, have not yet been identified. The insalubrity of some parts of the African coast, of the Pontine Marshes, and without going even so far, the crowded and generally ill-drained and ill-ventilated parts of our cities, intra-mural church-yards, all of which are the fertile and proximate cause of typhus and other fearful plagues, leave no doubt of the existence as well as deleteriousness of the substances which result from the putrefaction of animal and vegetable matter, and which is soluble in water, for MM. Thénard and Dupuytren have ascertained that pure distilled water kept for a while in dissecting-rooms becomes turbid, and rapidly exhales a fetid smell; and it should be observed that the atmosphere of dissecting-rooms is generally much less contaminated than that of several metropolitan or city districts. The presence of organic bodies in the air, and which vitiate its purity, is easily ascertained by putting some ice in a vessel, and placing it in such an atmosphere; the water which condenses on the surface of the vessel which contains the ice rapidly undergoes putrefaction from the organic substances which it (the condensed water) holds in solution.—ED.

to show how the chemical combination of hydrogen and nitrogen, called ammonia, can be separated from other substances. This is very often attended with many difficulties. The method which yields the most accurate results for the analysis of ammoniacal combinations, consists in determining the substances which are combined with the ammonia, and deducting afterwards the quantity of the latter from the loss. As I have fully treated before of the quantitative determination of the inorganic acids, I need not explain here the process to be adopted for determining in ammoniacal soluble salts, the quantity of the acid which is combined with the ammonia.

When the quantity of acid combined with ammonia in a weighed quantity of ammoniacal salt has been determined the loss in weight indicates only the collective quantity of the ammonia and of the water contained in the salt. Most of the combinations which ammonia forms with the oxacids contain water, a portion of which, at least, is always essential to the existence of the salt, and cannot be removed without decomposing the latter.

\* The most accurate method of determining immediately the quantity of ammonia contained in ammoniacal salts consists in combining it with muriatic acid, and converting the muriatic acid of ammonia into an insoluble ammonio-chloride of platinum, by means of chloride of platinum. If the ammoniacal salt is soluble in alcohol, to the alcoholic solution of a weighed quantity of the salt an alcoholic solution of chloride of platinum and a little muriatic acid are added, which produces immediately a double chloride, which at once falls down. The less water the alcohol employed contains, the more complete is the separation of the double chloride. To render this separation as complete as possible, one-fourth or one-fifth of ether should be added to the alcohol. The precipitation is best effected in a bottle capable of being closed, especially because the whole should be left at rest for twelve hours, in order that the precipitate may settle well. The precipitate is afterwards washed with alcohol. If a

weighed filter has been used, the quantity of ammonia contained in the dry double salt may be calculated by means of the tables.

\* It is more exact, however, and much more expeditious to convert the double salt, by ignition, into metallic platinum, which is then to be weighed, and from which the quantity of ammonia existing in the salt may be calculated by means of the tables. A weighed filter need not, of course, be employed then. Yet, if the ignition of the double salt is not performed with care, the fumes of muriate of ammonia and of chlorine easily carry away a small quantity of undecomposed salt, and even a little metallic platinum.

\* This loss is avoided by not removing the salt from the filter before igniting it, but wrapping it in it and exposing the whole for a long time, to a moderate heat, in a closed platinum crucible. The filter becomes slowly charred, and nothing but muriate of ammonia and chlorine are evolved, whilst not a particle of undecomposed salt is mechanically carried away. It is indeed difficult to incinerate the carbon of the filter, but all loss of platinum is, on the other hand, completely avoided.

\* If the ammoniacal salt is soluble in water, but is insoluble in alcohol, to a solution of the salt, as concentrated as possible, a little muriatic acid is first added, and then an alcoholic solution of chloride of platinum, and, lastly, a considerable proportion of very strong alcohol, mixed with ether. The double salt separates, and it is washed with alcohol. When the ammoniacal salt is soluble in water, the acid which it contains is always soluble in alcohol, even that which is mixed with ether.

\* When ammonia, or an ammoniacal salt, is contained in a very dilute aqueous solution, a suitable quantity of a solution of chloride of platinum and of muriatic acid is added thereto, and the whole is evaporated to dryness at a very gentle heat, after which alcohol mixed with ether is poured upon the dry residuum, and

the double salt of ammonia and platinum is collected on a filter.

\* If the ammoniacal salt is soluble in water, but mixed with other salts which contain no ammonia, and if the latter are soluble in water, but insoluble in alcohol, and yet if their bases do not produce, when treated by chloride of platinum, insoluble or sparingly soluble double salts, these salts fall down along with the insoluble double salt, when the experiment is performed as above said. The precipitate is washed with alcohol, and treated in the same manner as the double salt alone; the ignited combination is then put in the platinum crucible, water is poured upon it, which leaves the platinum in a very fine state of division, whilst the other salts are dissolved. The great specific gravity of platinum renders its separation extremely easy, especially by adding a little muriatic acid to the water, and applying heat; the supernatant liquor is easily decanted, water is then poured upon it again, until all the salts have dissolved, and pure platinum remains. It is then dried, ignited and weighed.

If, on the contrary, the ammoniacal combination is insoluble in water, it can sometimes be dissolved in muriatic acid, and the process is the same as I have just described; at other times the ammonia can be disengaged in the gaseous state from its combination, by means of a strong base, and it may then be dissolved in muriatic acid, and converted into ammonio-chloride of platinum, insoluble in alcohol, by means of chloride of platinum.

\* Hydrate of baryta is in most cases preferred for effecting the decomposition of the ammoniacal combination. If lime were employed instead, the retorts would very often break on applying heat. But a mixture of hydrate of lime with a great deal of hydrate of baryta may often be used.

\* The combination is weighed in a small retort of thick glass.



difficult of fusion, and capable of bearing variations of temperature without breaking. A large excess of hydrate of baryta, or a mixture of hydrate of lime and baryta, is then introduced into the retort, the whole is well mixed by stirring, and the mixture is covered with hydrate of baryta. The neck of the retort is then drawn out to a long thin point, which is led into a small bottle half filled with water. The point of the retort must be at a distance of one-fourth or one-half of an inch from the surface of the liquid. The neck of the retort penetrates into the bottle through a cork traversed likewise by a glass tube connected with a second bottle which contains concentrated muriatic acid, and below the level of which this tube plunges. The retort and the first and second bottle are well luted and joined together, but the second bottle is not closed air-tight.

\* The retort is then heated. The current of ammoniacal gas which disengages passes into the first bottle, and is dissolved by the water which it contains; a little common air only escapes from the acid of the second bottle; the small quantity of ammonia which it contains is dissolved by the acid, above the surface of which, faint white clouds of muriate of ammonia are seen floating, but not a particle of which escapes from the flask.

\* When no more ammonia is evolved from the retort, the heat is withdrawn. The operator knows that the disengagement of the volatile alkali has ceased, when the water which escapes from the hydrate along with the ammonia remains in the neck, and endeavours to go back into it at the slightest cooling of the retort. The water which is thus simultaneously disengaged carries away all the ammonia in the bottle, none of which remains in the retort.

\* As soon as the retort cools, the acid ascends from the second flask into the first, and fills the empty portion of the latter with clouds of muriate of ammonia. The operator then hastens to fuse the long and thin point of the retort. When the clouds have dissolved in the water, the contents of the first flask, and the portion of acid which has gone back into the second, are

mixed together, and an excess of a solution of chloride of platinum is added to the whole. The liquor is then evaporated very slowly by the water-bath, nearly to dryness, and anhydrous alcohol is poured upon the residuum. The insoluble double salt which has been produced is collected on a filter, it is washed with alcohol in order to remove the adhering chloride of platinum, and it is treated as above.

\* This method may sometimes be resorted to for the analysis of the bodies called amides, in which the treatment by hydrate of baryta or of lime produces ammonia, the quantity of which may thus be very well determined.

\* When ammonia is to be disengaged from its solutions by this method, an apparatus of a similar construction is employed to determine its quantity; except that the solution is put in a larger tubulated retort, or in a matras where it is mixed with hydrate of baryta or of lime. If the latter substance is employed, the mass froths up very much, and may even pass out of the vessel; wherefore, hydrate of baryta is preferable. The liquid is kept boiling until half the water has distilled over. This method may be adopted for the quantitative determination of the ammonia of mineral waters, after having carefully concentrated them by evaporation in the water-bath.

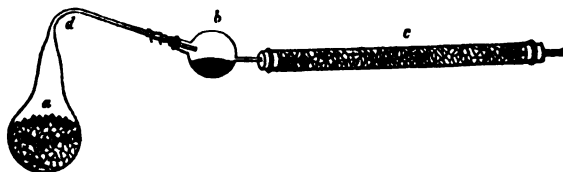
\* The quantity of ammonia contained in solid compounds, may also be determined by means of a method which will be described farther on, that is to say, by protoxyde of copper (*oxyde cuivrique*) as is practised for organic compounds. The ammonia is thus converted into nitrogen gas, which is measured, and into water, which is weighed. It is difficult in these experiments to obtain the nitrogen gas free from all traces of nitric oxide. The production of the latter should be prevented by mixing very finely divided metallic copper with the protoxyde of this metal. When ammoniacal gas is mixed with other gases which are not absorbed by water, this method of

separation may be used. Dry chlorine gas, however, separates ammoniacal gas very well from all the other gases with which it is mixed.

**\* DETERMINATION OF WATER IN AMMONIACAL COMBINATIONS.**

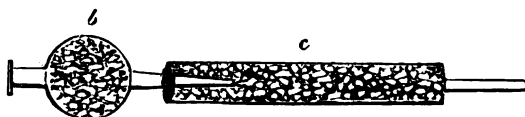
When a known weight of an ammoniacal salt is decomposed by a weighed quantity of a strong anhydrous base, with the help of heat, the increase of weight of the base added indicates the quantity of the acid which was combined with the ammonia, provided this acid does not form, with the base employed, a combination which heat can destroy. The loss of weight represents the collective quantity of the water and ammonia.

If the operator wishes to determine the quantity of ammonia from the loss, and to estimate immediately that of the water liberated, the following process may be followed. The quantity of ammoniacal salt evolved in the experiment is introduced into a small matras, as here represented. But as this matras must be of very strong glass it cannot be made by blowing a glass tube; it must be procured from the glass-house. If, however,



such a flask cannot be had, a small retort may be employed. After having taken the weight of the matras or of the retort, a suitable quantity of the salt, reduced into fine powder, is introduced into it, and the neck of the vessel is cleaned with the feather of a quill; the apparatus is then weighed a second time, in order to know exactly the weight of the substance experimented upon. This being done, pure lime in powder

is introduced into the retort, for which purpose calcined Carrara marble is best, and rather more than double the weight of the ammoniacal salt is employed. The two substances are mixed together as intimately as possible by shaking the matras, and the whole is again rapidly weighed. The neck of the retort is then drawn out to a long point and bent, so as to give the vessel the shape of a retort. If a retort is employed, the neck thereof must likewise be drawn out to a point, which being done, the matras or the retort is again weighed for the fourth time. A small receiver, *b*, similar to that represented here, is adapted to



the neck of the retort by a tube of caoutchouc. This receiver is filled with lumps of hydrate of potash, and connected to a small glass tube *c*, filled also with hydrate of potash. The tube *c* and the receiver *b*, with the tube of caoutchouc, are weighed before the experiment.

The apparatus being ready, the glass bulb is gradually heated, and the heat is afterwards increased as much as possible. The ammonia gas very soon disengages, but a portion of the water is obstinately retained by the excess of lime employed, and by the salt of lime which has been produced, and is disengaged only by heating the retort as strongly as possible. When this bulb is of a very small diameter, the ignition can be performed over an argand spirit-lamp, but when it is larger it must be heated over a charcoal fire. After cooling, the neck of the retort is cut at *d*, and its weight is taken. The receiver is weighed also with the glass tube and the point of the retort, which point is then dried and weighed separately, and its weight is deducted from that of the receiver and of the glass tube, and it is added to that of the retort. The loss sustained by the retort after ignition consists of the collective weight of the ammonia and the water. The increase of weight of the hydrate of potash indicates the quantity

of water contained in the ammoniacal salt experimented upon, and from which that of the ammonia is calculated.

This experiment is attended with a disagreeable circumstance, namely, that the heat required to expel completely the water from the retort must be so strong that the glass is very often softened by it. If the experiment is performed over a naked fire it may happen also that after cooling, the retort cannot be accurately weighed, which, however, must absolutely be done. Now, as at the beginning of the experiment, the whole of the ammonia has been disengaged by a gentle heat, and as it is only the complete expulsion of the water, which requires a very high temperature, the experiment had better be performed in the following manner:—The retort is exposed only to the flame of an argand spirit-lamp, and after cooling its weight is determined, and also that of the receiver and of the glass tube, as was just said. The loss of weight sustained by the retort indicates the quantity of all the ammonia and of a portion of the water which was absorbed by the hydrate of potash; if the increase of weight of the hydrate of potash is deducted from the loss of weight experienced by the retort, the difference indicates very accurately the quantity of the ammonia which existed in the salt experimented upon.

When the quantity of ammoniacal salt experimented upon is small, and does not exceed, for example, one or two grammes, it is not necessary to connect the receiver *b*. The neck of the retort may at once be immediately passed through the cork into the tube filled with hydrate of potash.

\* Pure protoxyde of lead, recently calcined and pulverised, is preferable to lime in such experiments, for an excess of this body is far from retaining the water so strongly as lime, so that a moderate heat is sufficient to expel it completely.

If, by applying a very strong heat, the whole of the water of the salt of lime were expelled, the operator might at once and

immediately determine both the quantity of the water and of ammonia. To do this the neck of the retort should be connected with a glass tube, filled with hydrate of potash, and the latter should be united by means of a ring of caoutchouc with another glass tube full of fused chloride of calcium. The two glass tubes should be weighed, each separately, before the experiment. The increase of weight of the hydrate of potash will then indicate the quantity of the water, and the increase of weight of the chloride of calcium would show the quantity of the ammonia contained in the ammoniacal salt employed. But whether an accurate result can thus be obtained has not yet been proved by experiment.

In some cases the quantity of the water and of the ammonia contained in a salt can be collectively determined by the decrease of weight sustained by igniting it. This is the case with some of the double salts, which an ammoniacal salt produces when it combines with another salt having a fixed base; the result of the ignition is, that the acid of the ammoniacal salt combines with the salt which has a fixed base, and this produces an acid salt. Such is the case, for example, with the double salts, which result from the combination of phosphate or arseniate of ammonia with other phosphates and arseniates.

It is possible, also, by a slight ignition in open vessels, to determine collectively the quantity of water and of ammonia contained in ammoniacal salts, the acid of which, even in state of purity, is completely refractory, or at least is not decomposed by a very strong heat. Such is the case with the combinations of ammonia with titanous, molybdic, tungstic, antimonous, antimonious, tantalic acids, &c. A few of these combinations, when ignited out of the contact of the air, react by their ammonia, which undergoes decomposition, upon the acid, which is thereby converted into a lower degree of oxydisation.

\* The methods which have been described serve to analyse

not only the combinations of the oxacids with ammonia, but those also of the hydracids with this alkali. Although the latter combination contains no water of crystallisation, it is known that when they are decomposed by bases, the oxygen of the latter and the hydrogen of the hydracids form water. These combinations produce, therefore, during the quantitative determination of their constituents, the same phenomena as the ammoniacal salts formed by the oxacids.

SEPARATION OF HYDROGEN FROM CHLORINE, BROMINE, IODINE,  
AND CYANOGEN.

The combinations of hydrogen with chlorine, bromine, iodine, and cyanogen, or with hydrochloric, hydrobromic, hydriodic, and hydrocyanic acids, are determined quantitatively in their aqueous solutions by the methods which have already been partially explained before. Muriatic acid is precipitated by nitrate of silver; the latter reagent must also be employed for precipitating hydrobromic, hydriodic, and hydrocyanic acids. I have already said (pages 574, 601, 606) how the combinations of silver with chlorine, bromine, and iodine, must be subsequently treated. With respect to cyanuret of silver, after collecting it upon a weighed filter and drying it, its weight may be determined, from which the quantity of the hydrocyanic acid may be estimated. It is, however, quite as accurate to convert it into silver by ignition, and to calculate the quantity of the cyanuret of silver from the weight of the metal, and to deduce from this quantity that of the hydrocyanic acid. In the latter case no muriatic acid must be present with the hydrocyanic acid. The method which I have just indicated for the quantitative determination of the latter acid, yields a much more accurate result than another method which is frequently employed, and which consists in first adding a solution of potash to the aqueous hydrocyanic acid, then adding a solution of iron containing this metal simultaneously in the state of protoxyde and of peroxyde, and lastly adding dilute muriatic acid. From the quantity of

prussian blue produced, the quantity of the hydrocyanic is calculated. The results given by this method are all inaccurate.

When muriatic acid gas is mixed with other gases completely insoluble in water, they may be separated by this menstruum which absorbs it immediately and completely. It may also be separated from carbonic acid gas by passing into the gas mixture through mercury, pieces of borax, which absorb muriatic acid gas, and have no action upon the carbonic acid.

#### SEPARATION OF HYDROGEN FROM CARBON, AND CARBURETS HYDROGEN FROM OTHER GASES.

The combinations of carbon with hydrogen are either gaseous, liquid, or solid. They are often found mixed together, but it is then difficult to separate them. When a mixture of the gaseous combinations of hydrogen and carbon, namely, dicarburet of hydrogen (gas of marshes—*carbure tetrahydrique*) and bicarburet of hydrogen (olefiant gas—*carbure dihydrique*) is met with, which is the case with the gas-light obtained by distillation of coals or of oil, they may be separated from each other, according to Henry, by treating them by gaseous chlorine. Chlorine gas, in the dark, combines only with the olefiant gas (*carbure dihydrique*), and produces chlorinated ether (*ether chloré*); under the influence of solar light, it combines with the dicarburet of hydrogen (*carbure tetrahydrique*), producing muriatic acid and carbonic acid. The separation of the carburets of hydrogen by means of chlorine gas, can obviously take place over water only, and not over mercury, which would absorb the chlorine. The operator begins first by passing chlorine over the water-trough into a graduated tube, and the volume is measured; the gaseous mixture under examination and which has been previously measured in another graduated tube, is then introduced into it. The larger the proportion of olefiant gas contained in the mixture is, the less chlorine must be employed, because one volume of the latter gas is sufficient



to produce chlorinated ether with one volume of olefiant gas. In order that the reaction of the chlorine may take place in the dark, the best is to inclose the glass tube in a pasteboard sheath or case; which precaution, however, is almost superfluous when operating by candle-light. When the mixture has been left at rest for a quarter of an hour, all the chlorinated ether has separated. The operator then calculates, from the total diminution of volume, that of the olefiant gas, since the latter forms half the volume of the gas which has disappeared. The mixture is then exposed to solar light, or only to daylight, and the dicarburet of hydrogen (*carbure tetrahydrique*) is then converted, by the chlorine, into muriatic acid, which is immediately absorbed by the water, and into carbonic acid. This conversion is more rapidly effected under the influence of solar light than under that of diffused light. If an excess of chlorine gas has been employed in this experiment, after solution, the remaining gas, which consists of chlorine and of carbonic acid, is completely absorbed by a solution of potash. This phenomenon does not take place when too little chlorine has been employed, for oxyde of carbon only is produced, which is not absorbed by a solution of potash; neither does it take place when the gaseous mixture operated upon contains other gases besides. Four volumes of chlorine gas are required to convert one volume of dicarburet of hydrogen (*carbure tetrahydrique*) into carbonic acid and muriatic acid.

This method of analysis cannot give results as accurate as those obtained in other analyses of gases. As the experiment must be performed over water, into which carbonic acid and chlorine are soluble, the volume cannot be rigorously measured. If, on the contrary, water saturated with chlorine is employed, chlorinated ether begins to be formed the very instant that the gaseous mixture to be examined is passed through, and, moreover, after the absorption of the olefiant gas, a little chlorinated ether gas is formed, which augments the volume of the gas which has not been absorbed in the dark.

If, after having introduced a mixture of one volume of dicarburetted hydrogen (*carbure tétrahydrigue*) with rather more than double its weight of oxygen into a tube like that described (page 677), an electric spark is passed through it, it explodes, and is converted into water and carbonic acid. The carbonic acid formed has exactly the same volume as the carburet of hydrogen experimented upon. After the explosion, the volume of the carbonic acid obtained is determined by means of hydrate of potash in the ordinary way, by which means it is separated from the excess of oxygen employed.

If a volume of carburetted hydrogen (olefiant gas) is exploded in the same manner, with rather more than three times its weight of oxygen, it is also completely converted into water and carbonic acid; but the volume of the carbonic acid produced is double that of the carburetted hydrogen gas employed.

If a gaseous mixture is composed of the two gaseous carburets of hydrogen, the operator may very easily, from the carbonic acid obtained, find the relative proportion of the two carburets, provided the volume of the mixture has been accurately determined beforehand. As soon as the decomposition is effected, hydrate of potash is introduced into the gas, and from the diminution of volume, that of the carbonic acid produced is determined, which should always be more considerable than that of the gaseous mixture experimented upon. The excess corresponds precisely to the volume of the olefiant gas contained in the gaseous mixture, and it gives at the same time the volume of the dicarburet of hydrogen. If, for example, the gaseous mixture is fifty volumes, and the carbonic acid gas eighty volumes, the gaseous mixture contains thirty volumes of olefiant gas (*carbure dihydrique*), and twenty volumes of dicarburet of hydrogen (*carbure tétrahydrigue*).

This experiment, however, is dangerous, especially when the gaseous mixture contains much olefiant gas, for its decompo-

sition is accompanied by so violent an explosion, that the thickest tubes may be easily broken. Only a small quantity of gas should, therefore, be detonated at a time, and previously to exploding it, the glass tube should be wrapped up in a towel.

When the gaseous mixture contains free hydrogen, this experiment does not yield accurate results.

The gaseous mixture of the two carburets of hydrogen may contain also free hydrogen, carbonic oxyde, carbonic acid, and nitrogen. Such mixtures occur in the gaseous products of the distillation of coals, and of the impure fatty bodies employed for gas-light. These gases may be separated from each other in the following manner:—The volume of the mixture is first accurately determined over the mercurial trough, and the carbonic acid is absorbed by a small quantity of hydrate of potash, which is to be introduced by means of an iron wire into the gas through the mercury; the potash is then withdrawn, and the quantity of the carbonic acid gas is determined from the diminution of the volume. The glass tube is then to be held in an inclined position, and potassium, previously heated, is then introduced to the upper part of the tube. The potassium, if in sufficient quantity, combines with the oxyde of carbon, and has no action upon the other gases. From the diminution of the volume of the gaseous mixture those of the carbonic oxyde may be determined. A measured volume of the remaining gas is then treated over water, in the dark, by gaseous chlorine, as was said before, and the olefiant gas alone is absorbed. The remaining gas is then treated in the diffused light by gaseous chlorine, which combines with the dicarburet of hydrogen (*carbure tétrahydrigue*), and with the hydrogen. The rays of the sun must be avoided, for an explosion might thus be produced if the mixture contained much free hydrogen. The dicarburet of hydrogen then leaves carbonic acid, and the muriatic acid produced by the chlorine is absorbed by water, and the carbonic acid is absorbed by potash in the usual way, and its volume is

determined. The quantity of the dicarburet of hydrogen becomes thus known, since its volume is equal to that of the carbonic acid formed. The residuum is nitrogen gas, which is measured. The loss indicates the volume of the hydrogen gas.

It is easily perceived that the results obtained by this method are only an approximation to truth, and are often very inaccurate; but as the analysis of such gaseous mixtures is scarcely ever made otherwise than for technical purposes, the method is sufficiently exact.

If the carburetted hydrogen is not mixed with all these gases but with some of them only, the analysis may be made in a more simple manner. The gas of marshes, besides dicarburet of hydrogen, generally contains also carbonic acid, atmospheric air, or rather, oxygen and nitrogen gases. The volume of the carbonic acid is found by absorbing it with potash; that of the oxygen is best determined in such cases by absorbing it with phosphorus, which must be introduced to the upper part of the tube after having withdrawn the potash. By decomposing afterwards, the carburet of hydrogen by means of chlorine gas in the dark, and removing the carbonic acid produced, and the excess of chlorine employed, by means of potash, that which remains is nitrogen gas.

The quantity of the carbon and that of the hydrogen contained in the numerous combinations of these two bodies is best determined by converting the compound, whether in the solid, liquid or even in the gaseous state, into water and carbonic acid, by combustion with oxide of copper. The method to be followed will be fully described farther on.

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Addition by M. E. Peligot:—

\* According to M. Jacquelin, hydrogen may be separated from the gaseous carburets of hydrogen by taking advantage of

the property which potassium possesses of absorbing completely the first of these two gases. The gaseous mixture is introduced into a curved bell over mercury, a piece of potassium is introduced into the curved or bent extremity, and a spirit-lamp is placed underneath and gradually raised higher, until the absorption begins, when it is left at the same height. If the temperature were too great, the hydrogen would escape, but on lowering the temperature it is absorbed again. M. Jacquelin has ascertained, by synthetic experiments, that the process is accurate.

\* If this method is really good, the above process, indicated by H. Rose, to separate by means of potassium the oxyde of carbon which is absorbed by this metal when mixed with hydrogen and other gases is not accurate, since potassium, it would appear, absorbs both oxyde of carbon and free hydrogen.

#### SEPARATION OF HYDROGEN FROM PHOSPHORUS.

The best method of analysing the gaseous combinations of hydrogen and phosphorus, consists in passing them over a weighed quantity of chloride or of dry sulphuret of copper, gently heated. The hydrogen of the phosphuretted hydrogen forms then with the chlorine, muriatic acid gas, or with the sulphur, sulphuretted hydrogen, which disengages, whilst the totality of the phosphorus remains combined with the copper. From the weight of the phosphuret of copper obtained, (in which the quantity of copper contained therein is known, because a weighed quantity of chloride or of sulphuret of copper has been used for the experiment), the composition of the phosphuretted hydrogen gas is calculated. The phosphuretted hydrogen gas, prepared by boiling phosphorus with alkaline solutions, always contains hydrogen in the state of simple mixture with it. Yet, sulphuret of copper is not at all attacked by hydrogen gas, and chloride of copper is attacked by it only at a higher temperature than that used in the experiment; which remark applies also to the resulting phosphuret of copper.

\* In order to separate the phosphuretted hydrogen from the hydrogen mixed with it, to determine the quantity of the latter, a solution of nitrate of silver or of perchloride of mercury (*chlorure mercurique*) is used, which absorbs the phosphuretted hydrogen, and leaves behind the hydrogen which accompanies it in the state of simple mixture. In this case, the gases must be treated over water; if the experiment was performed over mercury a concentrated solution of protosulphate of copper should be employed; but then, the decomposition of the phosphuretted hydrogen gas would take place much more slowly than with the solutions of the two other salts mentioned.

#### SEPARATION OF HYDROGEN FROM SULPHUR.

The gaseous combination of sulphur with hydrogen, called sulphuretted hydrogen, is quantitatively determined in the manner mentioned before, (page 387). If the volume of this compound existing in a gaseous mixture has to be determined, this gas may be absorbed by several substances. The best way is to proceed as for carbonic acid, namely, to employ a piece of moist hydrate of potash passed through mercury into the gaseous mixture, by means of a thin iron wire. The sulphuretted hydrogen gas is thus absorbed in toto.

But if the gaseous mixture contains other gases capable of being completely absorbed by hydrate of potash, as, for example, carbonic acid or other gaseous acids, acetate of lead strongly moistened with acetic acid is employed. A concentrated solution of acetate of lead, to which acetic acid has been added, may also be employed, carbonic acid gas not being absorbed by it.

\* *Another method* which is more suitable for separating sulphuretted hydrogen from carbonic acid, was indicated by Gay Lussac. After having measured the mixture of the two gases, the operator takes a glass rod a little longer than the graduated tube which contains the mixture. About one-third

part of this glass rod is then smeared over with starch paste, and rolled amongst finely pulverised peroxyde of manganese, which then adheres to the starch, and the rod thus prepared is then introduced into the glass tube. In a few minutes the sulphuretted hydrogen is completely absorbed. When the gas is too abundant, the glass rod may be withdrawn, again smeared over with fresh peroxyde of manganese, and again introduced into the tube. The carbonic acid remains, the volume of which may then be determined.

When the mixture contains muriatic acid gas, and sulphuretted hydrogen gas, a very small quantity of water might be resorted to as a means of separating them, for it would dissolve the first, and absorb the other in a much less considerable proportion. But as sulphuretted hydrogen is not insoluble in water, it is better to use borax, which was first proposed by Cluzel for separating the two gases. This salt absorbs slowly the muriatic acid gas, even when employed in lumps. As borax absorbs only the gases which are strongly acid, it may be resorted to also as a means of separating sulphurous acid from carbonic acid; but the method which consists in separating the two gases from each other by means of peroxyde of lead (*oxyde puce*), and which was described before (page 516), is preferable to this method.

In all experiments with sulphuretted hydrogen over mercury, the operator must not forget, that even in the cold this gas is slowly decomposed by mercury, which absorbs sulphur, and leaves hydrogen in the free state; which phenomenon takes place without producing any change in the volume.

When sulphuretted hydrogen exists in solution in a liquor, the best method of determining its quantity consists in pouring in the liquor a solution of a metallic oxyde, with which sulphuretted hydrogen may form an insoluble sulphuret, a solution of nitrate of silver or of proto-chloride of copper (*chlorure cuivrique*) may be employed for the purpose; acetate of lead is less suitable.

After having separated the sulphuret of silver or of copper, it is advisable to oxydise it completely by means of fuming nitric acid. The sulphuric acid produced is afterwards precipitated by a barytic salt in the state of sulphate of baryta, the weight of which is determined, and from which the quantity of the sulphuretted hydrogen is calculated. This method is every way preferable to that which consists in calculating the quantity of sulphuretted hydrogen by the weight of the metallic sulphurets; for if metallic chlorides should happen to be present, the solution of nitrate of silver would then produce a precipitate of chloride of silver along with the sulphuret of silver. It is true that this precipitation might be prevented by adding ammonia, but this alkali might, perhaps, precipitate other substances. I have said before (page 670), how this method may be applied to the determination of sulphuretted hydrogen in a mineral water.

#### SEPARATION OF HYDROGEN FROM SELENIUM AND FROM TELLURIUM.

The gaseous combinations of selenium and tellurium with hydrogen have so much resemblance with sulphuretted hydrogen that in order to determine them quantitatively, the same methods as those which are resorted to for the latter may be employed.

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#### ANALYSIS OF ORGANIC SUBSTANCES.

I have now to treat of the quantitative determination of the solid, liquid, and gaseous substances, which, besides hydrogen, contain carbon and oxygen, or carbon, oxygen, and nitrogen. They are called organic substances. The knowledge of their composition has become, of late years especially, a subject of considerable scientific interest. It is impossible in this manual to treat of the reduction of the organic bodies into their immediate principles, and I shall only treat of the methods by



which the operator is enabled to determine their mediate or remote constituents. This is done by oxydising their elementary principles; the hydrogen is converted into water, the carbon into carbonic acid, and is determined in the state of carbonic acid gas, the nitrogen is never oxydised, and must be obtained in the gaseous state. When the quantity of water produced has been exactly weighed, and the volume of the carbonic acid and nitrogen gases obtained has been measured, the operator may then find the composition of the substance operated upon by determining from the loss the quantity of oxygen which it contains, which generally is the best method.

\* The analysis of the substances which contain no nitrogen is more simple than that of nitrogenised bodies, and gives more accurate results. The determination of the quantity of the nitrogen is especially attended with difficulties when the substance under examination contains but little of it.

Gay Lussac, Thénard, and Berzelius formerly employed chlorate of potash to burn organic substances; but this salt is no longer employed now. The chlorate of potash was mixed with the substance to be analysed, and the mixture was ignited under the influence of heat; the elements entered into combination, each separately with the oxygen gas disengaged from the chlorate. Gay Lussac and Thénard, who performed the first accurate analysis of the kind, invented a very ingenious instrument for the purpose. But as, according to this method, the water produced cannot be immediately weighed, but the weight is estimated from the loss, the quantity of hydrogen contained in the substance submitted to analysis is always much less accurately ascertained than when the water produced is weighed. The instrument has, therefore, fallen into disuse.

Berzelius employed first combustion-tubes of glass, in which he burnt the organic substances, either alone, or more frequently united with a base which is ordinarily oxyde of lead. The

combustion was effected by means of chloride of potassium mixed with ten or twelve times its weight of chloride of sodium; but at a late period, and at the recommendation of Gay Lussac, I employed peroxyde of copper for burning it, and he then determined the weight of the water and of the carbonic acid produced.

\* Theodore de Saussure, instead of chlorate of potash or of oxyde of copper, employed oxygen for the analysis of nitrogenised bodies. As this gas undergoes no change of volume when it is converted into carbonic acid, the quantity of the hydrogen may be deduced by the diminution of volume after the combustion.

\* Prout and Herman employed, for their analysis, an apparatus in which the substances to be examined are burnt with peroxyde of copper, and which contains at the same time a determined volume of oxygen gas, which is passed and repassed over the peroxyde of copper, so that all the copper which has been reduced by the organic substance is brought back to the state of oxyde. If a substance contains oxygen and hydrogen in suitable proportions to form water, the volume of the oxygen gas employed is not altered. If a substance contains an excess of oxygen, the volume of this gas is larger after the experiment; it is, on the contrary, less if there is an excess of hydrogen.

\* Brunner has described also a very good apparatus grounded on the same principle.

\* The process which most chemists have adopted for the elementary analysis of organic substances, and which, in their opinion, is the simplest, and consequently the best and most convenient, is that of Liebig. There is, perhaps, no other method which requires less time, gives less trouble, and yields more accurate results; wherefore, I shall here merely describe the apparatus of the latter chemist, slightly, but not essentially, modified.

\* The course of the analysis varies according as the substance operated upon is composed only of carbon, hydrogen, and oxygen, or contains nitrogen besides. I shall treat first of the non-nitrogenised organic substances.

\* The substance experimented upon is solid or liquid, very volatile or non-volatile.

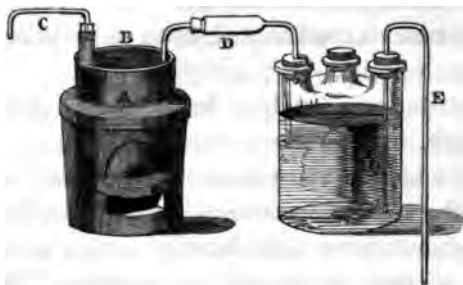
\* If the substance is solid, or but slightly volatile, a certain quantity, which, in most cases, need not be more than half a gramme, and which in many cases may be much less, is taken. If, however, the substance contains but very little hydrogen, and especially carbon, a more considerable portion must be taken, amounting sometimes to two or three grammes. If it be of an acid nature, and if it combine in definite proportion with fixed inorganic bases, one of its salts is taken in preference (provided it be not one of those which it forms with the alkalies or alkaline earths), and the quantity of the organic substance is accurately determined by the process which will be mentioned farther on.

\* A most essential condition is to take the organic substance in its utmost state of purity. Of all the foreign mixtures the hygroscopic water is that which is most troublesome to expel from pulverulent organic substances, which, however, is the case with all powders. The substance must be rendered as dry as possible, or, if it contained a determined quantity of water, it must not be accompanied by hygroscopic water.

\* I have already explained (page 630), how the quantity of water contained in substances is to be determined, and how the hygroscopic water can be eliminated. When, which is very often the case, an organic substance retains the water with great obstinacy, it may be completely removed in most cases by a current of dry air, but especially of hot and dry air. The apparatus employed for the purpose is as follows, and it has already been described (page 637).

The operator must take great care not to stop before he is quite sure that the exsiccation is complete, which is known

when water ceases to be condensed at the beginning of the tube D, and immediately before it. The operator weighs then the apparatus with the exsiccated substance, and the drying is con-

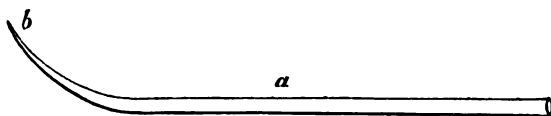


tinued until the two last weighings are exactly the same. In order to be more certain still that the substance is perfectly dry, a small quantity of it (after its weight has remained uniform) is poured in a long, narrow, and perfectly dry glass, in which, by means of a small spirit-lamp, it is exposed to a high temperature which, however, must not be so high as to decompose it. If it is seen that not a particle of water is deposited on the sides of the glass, the operator may rest assured that the substance has been dried completely. If the reverse is the case, instead of a water-bath, or of a bath of chloride of calcium, a sand-bath is employed in order to obtain a higher temperature, and dry air continues to be passed over the substance.

\* Fat and resinous substances, even when the latter are in fine powder, do not attract moisture, so that they may be weighed with great accuracy.

\* After having completely dried the substance, the quantity which is to be submitted to analysis is weighed. The weighing had better be effected in a covered platinum crucible which must not be too small, but which must be thin, and consequently light, and which must be counterpoised beforehand. When the cover fits well, the substance does not increase in weight during the short time employed in weighing.

\* If the substance can be obtained in the state of powder, it is in that state that it should always be employed. The powder is to be mixed with about thirty or forty grammes of peroxyde of copper finely pulverised, and previously ignited, and the whole is introduced in a glass tube. A tube of strong glass, difficult to fuse, and free from lead, is used for the purpose; it must be able to bear a dark red heat without fusing, and it must not be liable to break by being imprudently submitted to great variations of temperature. In the east of Germany,



where glass is generally made with potash, tubes of this kind are more easily procured than in the west of Germany, in England, and in France, where soda-glass is more generally employed. The tube *a* is about 18 inches long, and is about one-third of an inch in diameter; one of its extremities is drawn out to a point *b*, bent upwards.

The mixture being made, the tube is gradually heated, owing to which, the hydrogen of the substance is converted into water, and its carbon into carbonic acid, by the oxygen of the peroxyde of copper, which is thereby reduced into suboxyde of copper and metallic copper. The water and carbonic acid produced are weighed, and from their weight the quantity of the hydrogen and of the carbon contained in the substance is calculated; that of the oxygen is deducted from the loss.

\* Before introducing the substance into the combustion-tube, the latter must have been previously cleaned and dried. It should, accordingly, be well wiped with a piece of blotting-paper rolled at the extremity of a thick and strong iron wire, after which it must be heated, and the last traces of moisture are removed by plunging down to the extremity a thin glass tube through which the air is sucked up with the mouth.

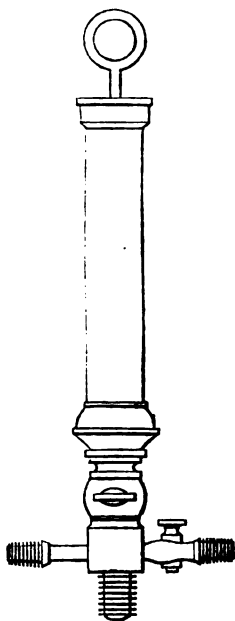
\* Before weighing the substance to be analysed, the peroxyde of copper, which will be used for the combustion, must previously be ignited, and a sufficient quantity of it is taken to almost entirely, but not quite, the capacity of the tube. It is then put into two small porcelain crucibles, and strongly ignited upon two argand spirit-lamps. The two crucibles are removed whilst hot, from over the lamps, and placed upon two glass covers containing a little mercury, and which are placed in a cap containing concentrated sulphuric acid, and the whole is covered by a bell. The peroxyde of copper which is thus cooled in a perfectly dry atmosphere, cannot absorb moisture.

When the peroxyde of copper has almost cooled, a little of the substance is to be mixed intimately in the platinum crucible itself, the substance which will have been weighed during that time. The whole is to be well stirred with a smooth glass-rod. If the substance is white, it is easy to see when the mixture is complete. More peroxyde of copper is gradually added; that is, as much as the crucible can hold, but so that it may as yet be mixed completely and intimately with the first mixture.

\* During that time the combustion-tube has been fastened in a vertical position between the cheeks of a holdfast, and a glass funnel having a neck as short and as large as possible has been placed over it, through which a quantity of pure and still unignited peroxyde of copper is poured, sufficient to fill about half the lower extremity of the tube, and, in order to prevent the mixture falling into the point *b*, and stopping it, a small portion of copper turnings, previously well ignited, are first projected into the tube. A little of the mixture contained in the platinum crucible is now poured through the funnel, avoiding with the greatest care the formation of dust; a little pure peroxyde of copper is then poured into it, and then a little of the mixture is further poured in, and then as the contents of the crucible gradually diminish, peroxyde of copper is added, so that towards the end, the mixture poured through the funnel contains a large proportion of peroxyde of copper. Enough peroxyde

copper must be reserved to fill about one inch of the length of the tube; it is used to rinse the crucible and the funnel, but a little must still be kept to fill the upper part of the tube.

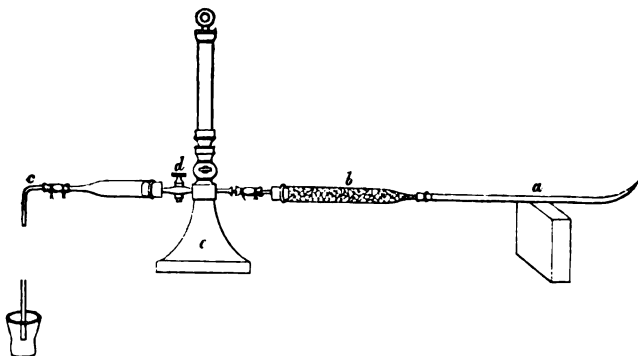
\* By operating thus, the necessity of mixing the substance with the peroxyde of copper in a mortar is avoided. If, however, a more precise mixture was absolutely required, as is frequently the case, it should be performed in an agate mortar, previously warmed. A little of the peroxyde of copper is first put in this mortar, and it is triturated as exactly as possible with the whole of the organic substance, and the remainder of the oxyde is gradually added. After having put, with a tube as described above, a layer of oxyde about half an inch in height, the mixture is poured in. The mortar and the crucible are then rinsed with the remainder of the peroxyde of copper, which thus forms the upper layer in the tube.



\* As during the mixing, especially if made slowly, the mixture might absorb traces of moisture, peroxyde of copper having a

greater tendency than many other pulverulent bodies to absorb hygroscopic moisture, which would unduly increase the quantity of hydrogen contained in the substance, a little air-pump, invented by Gay Lussac, is used for removing this moisture. The preceding figure represents the pump one-third of its natural size.

\* This pump is connected with the combustion-tube *a*, which communicates by means of a cork fitting air-tight with the glass tube *b*, full of chloride of calcium, as indicated in the next figure. The tube *b* is fixed to the pump by a tube of caoutchouc. At the two ends a little cotton is put before the chloride of calcium; *c* is a tube of glass about thirty inches long, fixed to the pump by means of a portion of a short and wide tube, the lower extremity of which plunges into mercury. The use of this tube is only to ascertain by the ascent of the mercury that all the joints are tight, and it is removed as soon as the pump begins to play. This tube may even be altogether dispensed with, for with a little practice the operator judges that the joints are tight from the ease with which the air penetrates the apparatus,



when, after having made the vacuum, the cock *d* is open; *e* is a strong wooden stand fastened to the table, and to which the pump is screwed.

\* By exhausting the combustion-tube the moisture contained in the peroxyde of copper mixed with the organic substance,

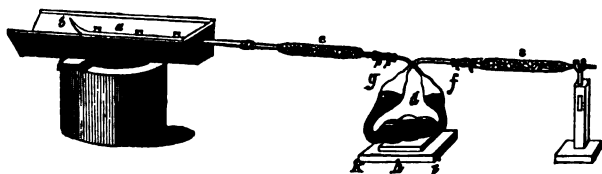


escapes with the air. The last trace of this moisture gradually disappears by opening the cock *d*, and exhausting the tube again, which then admits into the apparatus a fresh quantity of air, dried by the chloride of calcium.

The pumping must be performed cautiously, especially at the beginning, because by moving the piston too suddenly or too strongly, a little of the peroxyde of copper might be drawn from tube *a* into tube *b*. It is therefore necessary that the combustion-tube should not be filled too much with the mixture, so that a small empty space be left at the top. It is advisable also, in order to guard against the shifting of the peroxyde of copper, to put in the most anterior part of the tube some oxydised copper turnings which have retained their form.

\* It is evident that if the substance operated upon is such that there is no fear of loss from the action of heat, the expulsion of the moisture is greatly promoted by placing the combustion-tube in a tube of wrought iron containing hot water or hot sand.

\* When the hygroscopic moisture of the tube has been removed, the latter must be rapidly connected by means of a cork with a tube *c*, containing fused chloride of calcium, and



after having placed it in a small furnace, the tube *e* is connected with the apparatus *d*, which contains a very concentrated solution of hydrate of potash, for the purpose of absorbing the carbonic acid; *e* is a tube full of fused hydrate of potash, which, however, may, in most cases, be dispensed with, as will be shown farther on. All the joints are made of caoutchouc. The small

furnace is made of sheet-iron, and is open behind. The combustion-tube passes through a hole punched or cut into front side-piece; the lower part has a grate. The tube is supported upon small vertical pieces of sheet iron, hollowed out in middle, that it may lie firmly on them. The position of furnace is not perfectly horizontal, but it is inclined a little one side by means of a wedge, as shown in the figure.

\* The tube *c* is accurately weighed, as well as the apparatus containing the solution of potash. The latter weighs ordinarily between thirty and forty grammes, it may therefore be weighed in the small scales which are always used for analytical experiments. The solution of potash employed must have been prepared with pure hydrate of potash, and it must be concentrated, because otherwise the passage of the gas would create froth.

\* When the apparatus is ready, the combustion-tube is carefully heated by putting into the small furnace pieces of ignited charcoal, about the size of a large nut, the portion of the tube nearest the chloride of calcium is first heated, covering it with charcoal, and it is maintained at a red heat whilst the other portions of the tube are heated in the same manner. When the anterior portion of the peroxyde of copper begins to be heated, the portion of the mixture immediately behind is sheltered from the action of the heat by means of a small screen of sheet-iron, hollowed out so as to fit the combustion-tube. The screen of sheet-iron must be constantly employed in these combustions, when a portion of the tube is to be brought to a red heat before the remainder is strongly heated. The more slowly is the heat conducted, the more perfect is the combustion; the more slowly the disengagement of the carbonic acid takes place, the more accurate is the result of the experiment. When by using too strong a heat the disengagement of the gas is too rapid, it may be retarded by removing a few pieces of charcoal; but great care is still required, for the removal of too many pieces might cause suc-

lowering of the temperature that the solution of potash might ascend into the chloride of calcium tube.

\* Care must be taken also to place some ignited charcoal round the point *b* of the combustion-tube, when the portion of that tube which is nearest the chloride of calcium tube has been made red-hot, whilst the mixture itself has not yet been heated; for if the mixture was heated whilst the point *b*, and the peroxyde of copper which is quite near it, are cold, it might happen, especially if a volatile substance is present, that a portion of it would be volatilised and condensed into that point, whence it would be difficult to dislodge it.

\* From the small quantity of substance submitted to experiment, about an hour is sufficient to burn it completely. Ordinarily, however, when the substance contains much hydrogen and carbon, its combustion requires a longer time. If the glass of the combustion-tube is not very refractory, the stream of air in the furnace must be moderated by putting it, the furnace, upon stones, so that it may rest flat upon them.

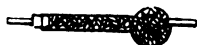
\* At the beginning of the experiment the solution of potash is placed in the apparatus for the reception of the carbonic acid, as in the above figure. As soon as the gas penetrates into the bulb *f*, the liquid rises into *g* of the bulb opposite, each bubble passing first into the bulbs *k*, *h*, and *i*, and it has still to overcome the weight of the column of liquid contained in the bulb *g*.

\* As soon as the combustion begins, the apparatus is placed in the position indicated in the figure, by means of a wooden support; its disposition must be such, that as soon as a bubble passes into *g*, it carries with it a certain portion of liquid, which, at each time, returns to its former horizontal position.

\* When the substance operated upon is a non-nitrogenised body, as soon as all the atmospheric air has been expelled by the carbonic acid, the liquor rises up to *g*, and remains at that

height during all the time of the experiment, because the whole of the gas is completely absorbed.

\* The water produced by the oxydisation of the hydrogen fixed by the chloride of calcium of the tube *c*. If the organic substance contains much hydrogen, and, consequently, if a large quantity of water is thus formed, it is necessary to employ a tube of the following shape :—



Almost all the water collects in the bulb, instead of spreading through the whole tube, from which it sometimes is liable to overflow. During the experiment, the water which deposits at the extremity of the combustion-tube is carefully driven, by means of a small spirit-lamp, towards, and into the chloride of calcium tube, which, if the necessary precaution is taken, is easily done without burning the cork. This cork, which connects the chloride of calcium tube with the combustion-tube, must be of good quality. Before using it, it should be softened by beating with a light hammer, which renders it more elastic. In order that it may fit quite air-tight, it should be somewhat difficult to force it into the orifice of the combustion-tube : as it is soft there is no risk of breaking the tube.

\* The combustion is at an end as soon as the disengagement of the gas ceases. If this disengagement ceases suddenly, the combustion is complete ; if, on the contrary, it becomes very slow towards the end, and continues still for a very long time the inference is, that the organic substance was not well mixed with the peroxyde of copper.

\* As soon as the operation is finished, the liquor rises into the bulb *f* ; the carbonic acid which this bulb contains being absorbed by the solution of potash, it would rise gradually into the tube *c*, which contains the chloride of calcium, and even at last into the combustion-tube *a*. To prevent this, a

soon as it has ascended a certain height into the bulb *f*, the point *b* of the combustion-tube is to be broken with pincers, after which the liquid falls immediately to a level; in order, then,



to obtain the carbonic acid which remains still in the combustion-tube *a*, and in the tube *c*, the operator sucks, with dry lips, a certain quantity of air through the potash solution, which absorbs the carbonic acid mixed with this air, whilst the chloride of calcium of the tube absorbs all the moisture which is still contained in the combustion-tube.

\* The increase of weight of the tube *c* indicates the quantity of water produced by the combustion, and that of the apparatus *d*, the quantity of the carbonic acid.

The tube *e*, full of fused hydrate of potash, is scarcely ever connected with the apparatus *d*, except when the substance under examination contains nitrogen. This tube serves to receive the moisture which might be mechanically carried away during the passage of the oxygen gas, and which would cause a loss of weight. It serves also to fix small quantities of carbonic acid which are mixed with the nitrogen gas.

\* Before surrounding the combustion-tube *a* with pieces of ignited charcoal, the operator must most carefully ascertain that all the joints, as well as the cork introduced into the combustion-tube, are air-tight. This is done as follows:—The apparatus being all connected, a certain quantity of air is sucked with dry lips, which makes the liquor, on account of the pressure produced, ascend to a certain height in the bulb *f*. If the level does not remain perfectly uniform for a quarter of an hour, the cork of the tube, or the tubes of caoutchouc, must be altered or replaced.

\* As by this apparatus the combustion of any quantity organic matter can be effected, since it is sufficient to lengthen the combustion-tube, the results arrived at are very accurate. But, I said before, in operating upon highly carbonaceous substances it is seldom necessary to take more than half a gramme, and if the substance is very poor in carbon, two or three grammes are generally sufficient.

\* If the substance to be analysed is very volatile, but in the solid state, the course of the analysis is as I have just described: only the layer of peroxyde of copper, just before the mixture of this oxide and of the organic substance, and which must be maintained at a red heat during the operation, must be thicker than is necessary when operating upon non-volatile substances. Especial care must be taken to heat the combustion-tube extremely slowly, and if the organic substance is very volatile, the combustion requires double the time employed for a non-volatile substance. If the tube were heated more rapidly a white cloud would often be perceived in the empty bulb of the potash-apparatus, which is a portion of the substance which has volatilised without being decomposed. As soon as this phenomenon is seen, the experiment is null.

\* It is necessary also, when, after having filled the combustion-tube with peroxyde of copper and the organic substance, the operator wishes to remove the hygroscopic moisture, to use the air-pump very cautiously, because frequent pumping might vitiate the accuracy of the result.

\* The mode of sucking the aqueous vapour and the carbonic acid of the apparatus, at the end of the experiment, has been objected to; but when this is done with dry lips, there is no fear of augmenting the weight of the potash-apparatus. Yet, in order to obviate this ground of objection, an aspiration-tube may be adapted, by means of a perforated cork, to the posterior orifice of the potash-apparatus.

\* It has also been proved by experiment that the dry atmospheric air which passes through the solution of potash does not take up ponderable quantities of water; which, however, can never take place whilst the small tube *e*, containing hydrate of potash, is employed.

\* At the end of the experiment, the operator, by breaking the point *b* of the combustion-tube, and then aspirating atmospheric air through the apparatus, may easily obtain a slight augmentation of the weight of the carbonic acid, because the air which penetrates into the apparatus contains much carbonic acid, produced by the combustion of the charcoal. This circumstance is avoided by taking care, in removing the charcoal at the posterior part of the combustion-tube, and breaking the point *b* to fit to the opening a tube about one foot and a half or two feet long, and into which pieces of hydrate of potash have previously been put, and which are kept in place by some cotton wool. The air aspirated passing through this tube before penetrating into the apparatus, is altogether deprived of its carbonic acid.

\* Finally, the chloride of calcium, which is to be put into the tube *c*, is also a subject of careful selection. When chloride of calcium has been kept for a long time in a state of fusion, in the air, in a platinum crucible, a very small portion thereof is decomposed by the moisture of the atmosphere; which, however, is the case with many metallic chlorides, the result being a formation of muriatic acid and of lime; the first escapes, whilst the second fuses with the undecomposed chloride. Now, such a chloride of calcium has the property of absorbing a little carbonic acid, which, in the combustion of organic substances, increases apparently the quantity of the water, and diminishes that of the carbonic acid. This defect is obviated by throwing a little muriate of ammonia over the chloride of calcium during its fusion, or by adding some muriatic acid,

keeping the crucible well covered pending the fusion, immediately pouring off the melted salt, in order to cool it.

\* There are some substances containing much carbon, such as coals, ulmine, indigo, and others of a like kind, which according to Liebig, cannot be analysed in a perfectly accurate manner in the way just described. The first impression of the heat disengages combustible gases from such bodies, and the gases reduce the peroxyde of copper near each small particle of the substance, so that there remains a great portion of carbon which can no longer be completely burnt. Hence, during combustion of these substances, the disengagement of gas goes on without stopping, and only becomes more slow, which may cause a loss of carbon amounting from three to ten per cent.

\* According to Liebig, chromate of lead may be employed to analyse these bodies. The quantity of chromate of lead mixed with the substance under examination must be half as much again as that of the peroxyde of copper.

\* When chromate of lead is used, it is necessary to give strong heat towards the end, which produces a disengagement of oxygen, which consumes the remainder of the carbon. If the tube employed is not one of very refractory glass, the strong heat used may cause it to bend or to collapse; this accident may, however, be guarded against by wrapping the tube with a sheet of thin copper, and binding it on three points with rings of twisted iron wire.

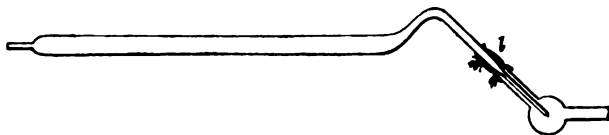
\* Chromate of lead may also be used with great advantage in the analysis of the organic substances which contain chlorine. If, instead of this salt, peroxyde of copper was employed, sulphide of copper would be formed, a portion of which might penetrate into the chloride of calcium tube, which would render the determination of the hydrogen defective. When chroma



of lead is used, basic chloride of lead is formed, which is less volatile than subchloride of copper.

\* Chromate of lead is obtained by precipitation, from a solution of a salt of lead, by means of a solution of bichromate of potash of commerce. The precipitate must be washed very carefully. After having dried it, it must be exposed to a very strong red heat until it softens or fuses, after which it is reduced into very fine powder. The ignition changes the yellow colour to a dirty reddish-brown colour. This salt may be employed in all cases in which peroxyde of copper is used; it has the advantage of not being hygroscopic, like peroxyde of copper, which renders it very suitable for the exact determination of hydrogen gas. An equal weight does not yield so much oxygen as peroxyde of copper, but an equal bulk contains half more oxygen.

\* Mitscherlich modified Liebig's apparatus so as to do without the cork to connect the combustion-tube and the chloride of calcium tube. The tube which he employs has the following shape:—



This tube, as is perceived, is bent at one of the extremities, which is turned towards the chloride of calcium tube, and is drawn out into a fine point; it is filled with peroxyde of copper, with which the organic substance has been mixed; but before introducing this oxyde, several small pieces of very fine copper turnings are pushed into the tube, in order to prevent the oxyde from passing into the bent portion. The posterior extremity is then sealed up, and drawn out to a point, as in Liebig's apparatus. The small point *e* is immediately connected to a chloride of calcium tube, in such a way that it penetrates amongst the pieces of this salt. This connection is made by

means of a tube of caoutchouc. The chloride of calcium is joined to the apparatus described (page 744), which contains a solution of potash, for the absorption of the carbonic acid. In order to determine the quantity of the water, after the experiment, the small point of the combustion-tube is cut immediately above the tube of caoutchouc, and the tube is then removed without withdrawing the point from the chloride of calcium to which latter tube is to be weighed with the point; it is then cleaned, and its weight is to be deducted from that previously obtained. Mitscherlich does not heat the combustion-tube immediately with charcoal: he places it first in a gun-barrel open in its whole length by means of a file.

\* When the organic body to be analysed is liquid, it must be put in glass bulbs, which are made of the shape represented in the figure. The neck is one inch or one inch and a half long



\* After having weighed the bulbs, they are heated, and the point is plunged into the liquid to be examined, which ascends into the bulb as the latter gradually cools. The point is withdrawn outside, and it is then sealed up with the lamp, after which the bulb is again weighed, which shows the weight of the liquid which it contains.

\* For ordinary volatile liquids, two bulbs capable of containing one-third of a gramme or half a gramme, are sufficient. The liquids which are less volatile are to be divided into three bulbs.

\* These bulbs are placed in layers, with the peroxyde of copper in the usual combustion-tube. The operator first puts one inch or one inch and a half of peroxyde of copper into the tube; he then takes one of the bulbs, and after having slight

filed the neck, he breaks the point off, and both the point and the bulb are let fall into the tube. The second bulb is treated in the same manner; this second bulb being separated from the first by a stratum of peroxyde of copper, two inches or two inches and a half long. The tube is then almost completely filled with oxyde in the ordinary way.

\* When the liquid to be examined is very volatile, the air must not be pumped out in the manner alluded to (page 739); the peroxyde of copper employed must be perfectly dry.

\* To effect this, the peroxyde of copper is to be ignited in the ordinary way, into two platinum crucibles, and it is poured, whilst almost red hot, in a glass tube of a diameter proportionate to that of the combustion-tube; it is then corked up with a perfectly dry cork, and allowed to cool. The size of the tube must be such, that the combustion-tube may be easily introduced into it. When the peroxyde of copper has become quite cold, the combustion-tube is plunged into that which contains the oxyde, and about one inch or one inch and a half of the oxyde is let fall, by turning the whole; then a bulb is introduced, then some more oxyde, then a bulb again, and the tube is next completely filled with oxyde, which is thus prevented from absorbing moisture.

\* If, however, the liquids operated upon are less volatile, the apparatus may be pumped as mentioned before (page 739). At each stroke of the piston, the bubble of atmospheric air contained in each bulb dilates and drives the liquid out of the bulb. The liquid is then immediately absorbed by the surrounding peroxyde of copper.

\* When the organic liquids submitted to analysis are not volatile, for example, fat oils, they may be weighed in a small glass tube, sealed at the bottom. This small tube is then introduced with the liquid in the combustion-tube, after having previously introduced about two inches of peroxyde of copper

into the tube. Inclining now the apparatus, the liquid flows out and is absorbed by the oxyde, which is gradually added and which mixes with the liquid; and, lastly, the tube completely filled in the usual way.

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Note by M. E. Peligot :—

\* MM. Dumas and Stas, in their experiments respecting the determination of the atomic weight of carbon, have indicated the imperfections of the process usually employed in organic analysis, and which consists in burning the substance by means of peroxyde of copper, collecting the water formed by means of chloride of calcium, and the carbonic acid by means of an aqueous solution of potash, then in passing a little air through the apparatus, in order that all the water and all the carbonic acid which it contains may be caught in their respective condensors. Although the composition of the organic compound determined by that method is exact in most cases, the dosing by weight of their elements is erroneous, and it is only by the help of fortuitous and variable compensations, that the true formula of the analysed bodies is arrived at. In effect, the carbon which was found in excess by calculation was lost during the analysis: since, according to the atomic weight, 76.4, the carbonic acid contained more carbon than is really the case, if, as there is no doubt, 75.0 is the true atomic weight of that body.

\* According to Messrs. Dumas and Stas there is a loss of carbon by that process.

1st., Because, in spite of all precautions, some portions of it are deposited here and there in the tubes, which, for want of oxygen, are not consumed.

2nd. Because the copper reduced is partly converted into carburet of copper.

3rd. Because the solution of potash suffers part of the carbonic acid to escape.

4th. Because the air which is aspirated through the apparatus carries away some water from the potash and diminishes its weight.

\* This loss of carbon may be avoided by means of the following modifications, through which the operator may arrive at rigorously accurate, and always constant results :—

\* The quantity of substance ordinarily employed, must be three times more considerable. The operator, for example, burns from 0·800 to 1·5 gramme of it, according as it is more or less rich in carbon and in hydrogen. When the analysis is finished, a large quantity of oxygen is passed into the tube, so as to burn the carbon completely, and to reoxydise all the copper, which decomposes the carburet of copper which had been formed.

\* The water is collected either into two U-shaped tubes, the one containing chloride of calcium, and the other minute fragments of pumice-stone moistened with concentrated sulphuric acid, or else in a single tube containing these two exsiccating substances, as represented in the following page.

\* By means of this arrangement the greater part of the water produced by the combustion of the organic matter is collected into the small closed and empty tube, 1. One of the limbs, 2, contains chloride of calcium, and the lower extremity contains pounded glass, over which the pumice-stone, moistened with



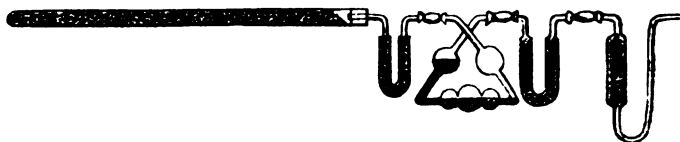
sulphuric acid, rests. The two small tubes are connected with the limbs of the U-shaped tube by means of corks sealed with red sealing-wax of the best quality, or by means of conical tubes of caoutchouc tied with annealed copper wires, which, for very

accurate experiments are much preferable to ligatures of silk or thread, the weight of which may undergo notable change during the experiment.

\* This apparatus may serve for several operations, taking care only to empty the small tube, in which the greatest part of the water has condensed.

\* Lastly, in order to absorb the carbonic acid, the bulb apparatus is filled with solution of potash at  $45^{\circ}$  of Baumé's areometer followed by a tube containing on one side pumice-stone moistened with a solution of potash, and on the other, dry potash. The object of the latter is to arrest the water which the gas might have absorbed.

\* The complete apparatus is represented here.



\* The combustion is carried on slowly as usual, and when terminated, the current of oxygen produced by the mixture of peroxide of copper and of chlorate of potash placed at the bottom of the tube, is disengaged. This being done, the combustion tube is removed with care, and it is replaced by a tube containing alkaline pumice-stone, and dry potash; by means of the last tube the air is aspirated, and it penetrates in a pure and dry state into the condensers, and replaces the atmosphere of oxygen which would otherwise augment their weight.

\* The combustion-tube must be about 60 or 70 centim. long, 10 or 12 centimetres of which are occupied by the mixture of peroxide of copper and of chlorate of potash; a column of oxygen about 8 centimetres long comes next, and then the mixture of the organic matter with the oxide of copper, which occupies about the same space, and the rest contains peroxide of copper.

\* M. Payen employs with advantage an apparatus in which the combustion-tube, to one of the extremities of which a tube of a smaller diameter has been soldered, is connected with a retort of refractory glass, containing fused chlorate of potash, for the purpose of supplying oxygen when the combustion, by means of the oxyde of copper, is terminated. The disengagement of the gas is more easily regulated by this arrangement than when the chlorate is put in the combustion-tube itself; but, with a little practice, the latter method of operating is not attended with any difficulty.

\* The glass of the combustion-tubes employed in France being generally too fusible, it is necessary to wrap them up in a strip of brass, or better still, of laminated red copper, coiled in a spiral round it, and strapped thereto by copper wire. The portion of the tube which contains the chlorate of potash, in MM. Dumas and Stas's process, and the other extremity in communication with the condensing apparatuses must alone be naked. M. Payen proposed to wrap the portion of the tube which contains the mixture of peroxyde of copper, and of the organic substance, in a metallic iron-wire cloth, which supports the softened glass better than the strip of copper, and which permits besides to watch the progress of the combustion, and of the oxydisation.

\* Respecting the determination of the atomic weight of organic substances, M. Rose says (page 774) "that an acid organic substance should never be combined with a fixed alkali nor with an alkaline earth, for the purpose of using the salt so produced for burning with the peroxyde of copper, even when it can be obtained in the crystalline state." There are, however, circumstances in which the organic analysis of these alkaline salts is useful or necessary, when the organic substance forms, with oxyde of lead or of silver, salts too easily altered, or when it can produce crystalline compounds with the alkalies only, or lastly, when from the stability of the latter salts, a state of exsiccation

can be obtained which is not attainable with its other compounds. It is true that in many cases, whenever the operator knows the elementary composition of the organic substance in a free state, and when this substance has not been altered by combining with the alkali, the dosing of the latter suffices to determine the composition of the salt, especially if this dosing can be performed accurately, which is the case with all the salts of baryta and of lime; the determination of organic elements becomes thus so much the less necessary, that it is always less exact than that of these bases.

\* Several methods have been proposed for the elementary analysis of this class of organic salts; some chemists admit that the base remains, after combustion, in the state of neutral carbonate, and add the carbon of this salt to that which has been fixed in the potash-apparatus in the state of carbonic acid. This method of proceeding is exceedingly defective, though it has been employed by very skilful chemists, amongst others M. Liebig, who used it, for example, to arrive at an erroneous determination of the composition of saccharate of baryta which had been accurately obtained before by dosing the base which it contains, which is easily done. In effect, after combustion, a portion of the alkali is found in the tube in a caustic state, either because the carbonate has been, at a certain epoch, partially decomposed by the aqueous vapour, or because the peroxyde of copper, at a high temperature, acts as an acid in displacing a portion of the carbonic acid of the carbonate.

\* M. Dumas having remarked that, in the analysis of tar emetic by peroxyde of copper, the whole of the carbon disengaged in the state of carbonic acid gas, recommends the use of antimonious acid, which being introduced into the combustion-tube with the alkaline organic salt and the peroxyde of copper, retains the whole of the base in the state of antimonious

\* M. Soubeiran endeavoured to determine all the carbon



saccharate of baryta by burning this salt by means of a mixture of chromate of lead, and bichromate of potash, both fused ; by using for 1 gramme of the organic compound, 100 grammes of chromate of lead, mixed with 10 grammes of bichromate of potash, he arrived at accurate results. Soubeiran's process may be useful in other cases.

\* Lastly, M. Gaultier de Glaubry proposed the use of phosphate of copper. As this salt must be in very fine powder, it should be dried by heating it in a capsula, only to the point at which it becomes yellowish-green. In that state, it still contains water, so that two organic analyses become necessary, the one without phosphate, in order to determine the water ; the other, in order to determine the carbon by adding a certain quantity of this salt to the mixture of oxyde of copper and of the organic substance in the proportion of 5 or 6 times the weight of the latter.—E. P.

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#### ANALYSES OF ORGANIC SUBSTANCES WHICH CONTAIN NITROGEN.

\* The analyses of this nature are attended with much more difficulty than that of non-nitrogenised substances. If the quantity of nitrogen in the substance is very small, if, for example, the volume of carbonic acid produced by the combustion with the oxyde of copper, is more than thirty or forty times that of the nitrogen gas, as is the case with the organic salifiable bases, the least quantity of atmospheric air sometimes produces notable discrepancies, because the nitrogen must be determined in the state of gas.

Another circumstance, which renders the determination of the nitrogen exceedingly difficult, is the production of nitric oxyde gas during the combustion of nitrogenised bodies by means of oxyde of copper, which production should be avoided. For, as nitrogen is always determined in the state of gas, and in volume,

and as when this gas is converted into nitric oxide its volume is doubled, the quantity of the nitrogen increases as soon as the state of gas) it contains nitric oxide gas.

\* The best method of preventing the production of nitric oxide, consists in using a combustion-tube of a larger size, in putting a layer, several inches long, of pure metallic copper before that of pure oxide, which must be put before the mixture of substance and of oxide. It is necessary, besides, to mix organic substance as intimately as possible with the oxide of copper, and it is advisable to employ for the purpose peroxide of copper, which has previously served for burning organic substances, and which consequently contains metallic copper and suboxide of copper. The combustion must be effected as slowly as possible, and, according to Liebig, it takes as much time again to burn it as that required for a non-nitrogenised organic substance.

\* The quantity of carbon and of hydrogen contained in a nitrogenised substance, is determined by a separate experiment as was directed before, respecting the substances which contain no nitrogen. During the combustion of nitrogenised bodies it is observed, that whilst it lasts, bubbles of gas escape through the potash apparatus without being absorbed. As soon as this phenomenon is perceived, the operator may rest assured that the substance contains nitrogen, and in pretty large quantity. This is ascertained better still, according to Liebig, by the odor of ammonia, which is produced by fusing a portion of the substance in a small glass, with from four to ten times the weight of hydrate of potash.

\* The method of determining the quantity of the nitrogen in organic substances, varies according to the percentage of the body. It is more simple when the quantity of the nitrogen is considerable. It is advisable, before determining the quantity of the nitrogen, to analyse the gaseous mixture obtained

burning the substance with oxyde of copper, and to examine what proportion the carbonic acid gas obtained bears to the nitrogen. In many cases this analysis of the gaseous mixture renders the ulterior quantitative determination of the nitrogen quite superfluous.

\* To effect this an unweighed portion of the organic nitrogenised substance to be examined, is mixed with a very large quantity of oxyde of copper, and the mixture is introduced into a combustion-tube, the posterior extremity of which has now been drawn out to a point, as represented in the figure (page 736). In the lower part of the tube, a little pure oxyde of copper is put, and the intimate mixture of the organic substance and of oxyde is next introduced, and covered with a stratum of pure oxyde a few inches thick, and, lastly, a stratum of copper turnings a few inches thick, and extending to the orifice, is poured in. The opening is then closed air-tight with a cork, through which the disengagement-tube passes and plunges in the mercurial trough. It is not necessary to remove the hygroscopic moisture of the mixture. The metallic copper and the anterior portion of the oxyde of copper are first brought to a strong red heat, and the operator then begins to ignite the mixture from backwards forwards, by surrounding the closed extremity with ignited charcoal. When the combustion of the substance has begun at that point, the atmospheric air is expelled from the apparatus by the gases which are disengaged. As soon as the operator believes that the air is about completely expelled, he begins to collect the gases in several graduated glass tubes, and he continues to heat the tube until gases cease to be evolved.

\* The first graduated tube having been filled with gas, rather more than half its capacity, atmospheric air is passed into it for the purpose of seeing whether any ruddy fumes will appear. The object of this experiment is to judge of the purity of the gas, and to ascertain whether it contains any nitric oxyde. When this phenomenon is observed, not only in the first

graduated tube, but even in the others, the combustion not been properly effected, and the experiment must be begun again, taking care this time to mix the organic substance intimately with the oxide of copper, or to increase the length of the stratum of metallic copper.

\* If the presence of nitric oxide is not indicated in the first or in the second tube, by the production of ruddy fumes introducing atmospheric air into it, the relative proportion of nitrogen and of carbonic acid gases is determined in the following tubes by plunging them, one after the other, in mercury until the level inside and outside is the same, after which the carbonic acid is absorbed by hydrate of potash. The remaining gas is pure nitrogen, the volume of which is determined, after having previously rendered it moist, if it has been deprived, of hydrate of potash, of the aqueous vapour which the mixture contained. It is better, however, to desiccate the gaseous mixture by means of chloride of calcium before absorbing it with hydrate of potash.

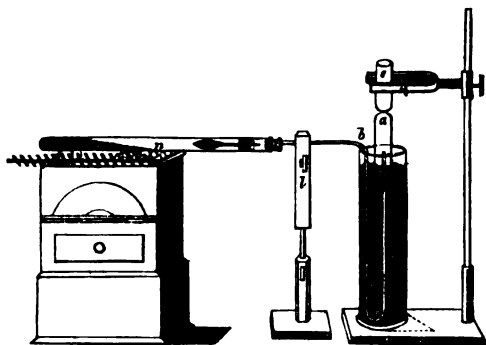
\* When, by means of a combustion effected in the ordinary way, the total quantity of the carbonic acid gas, or of the carbon contained in the substance, has been ascertained, it is easy to calculate also how much nitrogen it contained per cent for a volume of the carbonic acid obtained corresponds to one atom of carbon, and one volume of nitrogen corresponds to two atoms, or to a double atom of nitrogen. If, for example, one volume of carbonic acid and one volume of nitrogen have been obtained, the analysed substance contained, for 76.44 parts of carbon, 177.4 parts of nitrogen.

\* It is perceived that it is not necessary to proceed ulterior to the quantitative determination of the nitrogen in the substance, yet this method is safe only when the quantity of nitrogen in the substance examined is not too small, as

provided the relative proportion of this element to the carbon is not, according to Liebig, in a less ratio than 1 : 8.

\* In order to confirm the result obtained, an apparatus which was first employed by Gay Lussac and Liebig may be employed for the analysis of nitrogenised organic substances.

The graduated glass tube *a*, intended to receive the gaseous mixture, is placed in a glass vessel. The disengagement-tube *b*, which brings the gas in the graduated tube, has two vertical and parallel limbs, the ascending one of which reaches nearly to the



top of the graduated tube. When sunk to the utmost point, the other branch is outside of the glass tube. In order to render the disengagement-tube flexible, it may be cut at *b*, and the two parts may be connected by a tube of caoutchouc. After having filled the vessel with mercury, and engaged the conducting-tube within the graduated tube, the latter is depressed into the mercury, so as to expel through the conducting-tube all the atmospheric air that it contains; a certain quantity of which, however, remains. The glass tube is then fastened in that position by means of a clamp, or by putting a piece of cork, *c*, in the clamp, and keeping the tube down by pressing the cork upon it, as represented in the figure. The mercury of the graduated tube is adjusted at a perfect level with that in the glass vessel, and the volume of the atmospheric air which remains in the tube is accurately measured. The

combustion-tube *n*, which contains the intimate mixture of the substance to be examined, with the oxide of copper, and a very finely-comminuted metallic copper, is now adapted by means of a cork to the conducting-tube, placed between the arms of the support *l*. As soon as the mixture is decomposed the gas which is disengaged depresses the mercury into the graduated tube, wherefore, the clamp must be raised in proportion. When the decomposition is finished, the fire is removed and after complete cooling, the level of the mercury, inside and outside of the tube *a*, is again equalised. It is clear that the volume of gas which has penetrated in the graduated tube during the operation, corresponds exactly to the whole quantity of the gases which have been produced by the decomposition. As it is easy to ascertain, by another experiment, how much carbonic acid would have been produced in weight, by the quantity of the substance employed, and as it is likewise easy to calculate with the help of the tables, the volume of this gas in cubic centimetres, there is no difficulty in determining the volume and the weight of the nitrogen gas produced by the combustion.

\* The tube *n* should be cooled very cautiously, in order that it may not break, which, of course, would render the experiment void.

\* Gay Lussac and Liebig introduce afterwards, within the tube containing the mixture, that which contains the chloride of calcium intended to absorb the water, the latter being previously weighed. The tube full of chloride of calcium fits exactly the other tube, and that end of it which is towards the mixture is drawn out to a point. The tube containing the mixture is then closed up again by a cork, through which the conducting-tube passes, and it is placed naked upon the grate of iron wire supported by a furnace, the ash-hole and door of which are closed, and it is brought to a red heat by surrounding it with ignited charcoal.

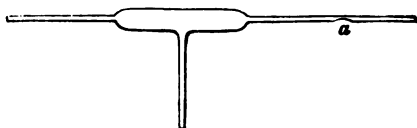
\* Instead of this furnace, it is better to employ one similar to

that used for ordinary combustions (page 741). It is, however, somewhat difficult with it to moderate the heat, so as to prevent the combustion-tube from softening, and from breaking on cooling, unless a plate of sheet-iron or bricks are placed under the grate of the small furnace.

\* The quantity of substance which may be analysed in this apparatus varies according to the capacity of the tube *a*. About 80 cubic centimetres of space are required for each decigramme of nitrogen presumed to exist in the substance, and 190 cubic centimetres for each decigramme of carbon.

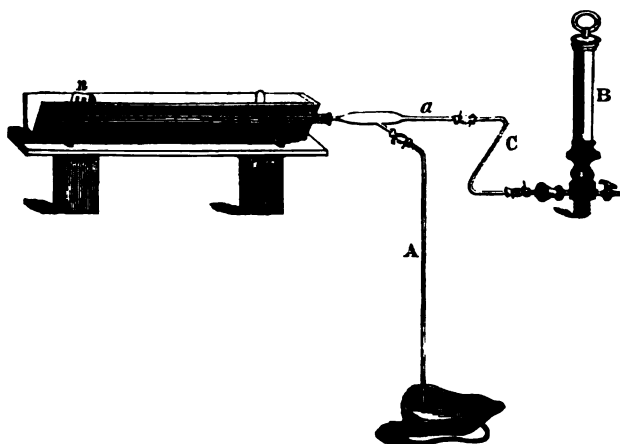
\* With respect to the substances which contain very little nitrogen, such as the organic salifiable bases, the whole quantity of the nitrogen may be determined by means of the following apparatus, which was contrived by Liebig:—Take a combustion-tube twenty-four inches long, which is not drawn out to a point but merely closed up in the usual manner. Introduce into it a layer, six inches long, of carbonate of copper, above which put a layer, two inches thick, of pure oxyde of copper, then the intimate mixture of the organic substance, with a large proportion of oxyde of copper; lastly, a layer of pure oxyde, and over this a layer of metallic copper turnings. The combustion-tube is connected by means of a cork to a three-limb tube, and the cork is luted with fused sealing-wax.

One of the limbs of the latter tube is connected by means of a tube of caoutchouc, with the pump B, which has been described (page 739); the other is connected, by means of a

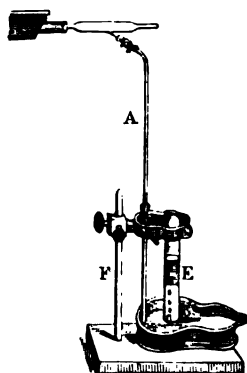


tube of caoutchouc, to a long glass tube bent at right angles, one of the limbs of which, A, must be thirty inches long, and plunge into a mercurial trough D. The three-limb tube is drawn out a little in *a*. By means of the pump, the air of the apparatus

is exhausted as much as possible, so that the mercury as into the tube A almost to the ordinary height of the baror. If the level of the mercury in the tube does not remain unal it is a proof that one or more of the joints are not tight.



\* The operator begins by gently heating the furthest end of the combustion-tube, that which contains the carbonaceous copper, and by means of a screen, *n*, the mixture is shielded from the radiating heat. A disengagement of carbonic



takes place immediately, which depresses the mercury in tube A, and the gas begins to escape through this tube. A vacuum is again made in the apparatus, and then by applyi



gentle heat, a little carbonic acid is again disengaged. This operation is repeated four or five times, or until the gas which escapes from the tube A into a test-tube, containing solution of potash, disappears completely. By means of a spirit-lamp, the drawn-out portion *a* of the three-limb tube is fused, and the portion C, and the pump B, to which it is connected, are removed. The graduated tube E is then fixed over the orifice of the tube A, by means of the stand and clamp F. The tube E has a capacity of about a hundred cubic centimetres, and it is half filled with mercury, and the other half with a concentrated solution of potash. The combustion of the organic substance is now begun, the gases which are disengaged, and which consist of carbonic acid, and of nitrogen, collect in the tube E, in which the carbonic acid is absorbed by the solution of potash, so that pure nitrogen only remains.

\* If the whole mixture of the organic substance, with the oxyde of copper, has been gradually brought to a red heat, whilst the anterior extremity, and especially the metallic copper, was maintained at a red heat, there must still be a reserve in the farthest extremity of the combustion-tube, of enough carbonate of copper to expel completely into the tube E, by means of the carbonic acid disengaged therefrom, the mixture of nitrogen and of carbonic acid contained in the apparatus.

\* As soon as all absorption has ceased in the tube E, it is closed with a flat piece of glass, and carried to a water-trough, the water of which takes the place of the mercury, and of the solution of potash. The quantity, and the volume of the gas is measured, after having observed the temperature, and the barometric pressure, taking into account the tension which the water exercises upon the volume of the gas reduced at a temperature of  $0^{\circ}$ , and at 0.76001 pressure, and the nitrogen may then be calculated in weight.

\* This method of expelling the atmospheric air by the carbonic acid disengaged from a metallic carbonate, was contrived by Dumas.

\* The use of the pumps may be thought by some to be useless in such experiments, by supposing that the carbonic acid disengaged at the beginning of the experiment, and before the combustion of the organic substance, must expel the atmospheric air of the apparatus; but such is not the case, for if the pump were dispensed with, the result would be notably inaccurate if the substance contained only a small portion of nitrogen.

\* When a non-nitrogenised organic substance, having decidedly acid character, or being capable of combining with bases in the manner of acids, is combined with ammonia for the purpose of forming a saline compound, and the relative proportions of the carbon and of the nitrogen contained in this ammonia salt is determined by the method described (page 759), the volume of the carbonic acid gas, and of the nitrogen gas obtained may be in a simple ratio, which confirms very well the determination of the carbon found by another analysis.

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Note by M. E. Peligot.

\* The quantitative determination of the nitrogen contained in organic substances is performed with accuracy and certainty by means of the process last described, provided the combustion tube employed be one metre at least in length, and be charged with a long column of ignited metallic copper, in order to decompose all the nitric oxide gas, which has a tendency to be produced. The copper used for this purpose must have been obtained from copper reduced from copper turnings, by means of hydrogen gas; the gas collected must always, after having been measured, be put in contact with a protosalt of iron, or with oxygen, in order to make sure that it contains no nitric oxide gas; a little air may also be introduced and the smallest traces of nitrous gas are then perceptible by the smell.

\* Instead of carbonate of copper white lead is often employed

for disengaging carbonic acid at the beginning and at the end of the experiment, but the latter substance as found in commerce, sometimes yields a small quantity of gas, which potash does not absorb, wherefore bicarbonate of soda has been advantageously substituted; it is only necessary to employ a larger proportion of this salt, for that found in commerce is never pure, and does not even part with half the carbonic acid which it contains.

\* MM. Will and Warrentrap have proposed also a method, the principle of which was first indicated by Berzelius, for determining, in the state of ammonio-chloride of platinum, the nitrogen contained in organic substances.

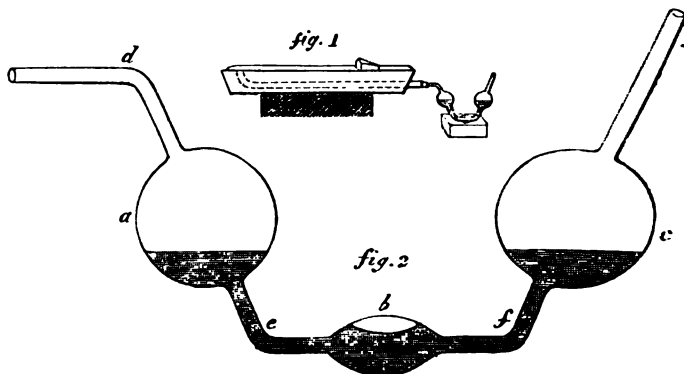
\* When an organic matter is heated with hydrate of potash, the hydrogen of this hydrate takes up the whole of the nitrogen of the substance, and forms ammonia. This reaction has been for a long time taken advantage of for detecting the presence or the absence of nitrogen in an organic product.

\* It has been proved by the direct experiments of the authors of this process, that, except for the substances in which nitrogen is contained in the state of nitric acid, all other nitrogenised substances, including the compounds of cyanogen, are decomposed under the influence of an excess of hydrate of alkali, and of a high temperature, in such a manner that the whole of the nitrogen is expelled in the state of ammonia.

\* The apparatus employed for this process is very simple; it consists, fig. 1, of a tube of hard glass, 45 or 50 centimetres long.

\* The extremity of the tube is drawn out and bent obliquely upwards. This tube, therefore, differs but little from an ordinary analytical tube, only it must be a little larger—about 20 or 25 centimetres in diameter. By means of a good cork, the orifice of the tube is connected with a bulb-apparatus containing muriatic acid. This tube is represented half its natural size in fig. 2.

\* This tube is filled by plunging one of its extremities muriatic acid of ordinary strength (sp. gr. 1.13), and by rating at the other extremity, *g*, until the liquid reaches level indicated in the figure.



\* For decomposing the nitrogenised matter, a mixture hydrate of potash or of soda, and of quick lime, is employed. The proportions must be such that the mixture cannot fuse at red heat, or at most that it should only slightly agglomerate. This mixture must be easy to pulverise, and must not absorb the moisture of the air too rapidly. MM. Will and Warrent use, in preference, one part of hydrate of soda mixed with two parts of quick lime.

\* The most convenient manner of obtaining this mixture consists in mixing a known quantity of quick lime with a corresponding quantity of alkaline ley of a known strength; the paste thus formed is ignited in a crucible, and then reduced into powder. Potash or soda, recently ignited, may also be pulverised in a warm mortar, and then mixed with finely-pulverised quick lime, obtained by calcining slaked lime. The perfectly dry mixture is kept in bottles having a wide mouth and glass-stoppered.

\* After having weighed the matter which is to be analysed, the combustion-tube, which must be very clean and dry, is placed

filled with the alkaline mixture, in order to have a determined measure of the quantity of hydrate which has to be mixed with the matter to be analysed, and the quantity of which latter substance must vary with the presumed amount of nitrogen contained in the substance. It is rarely necessary to employ more than 400 milligrammes of a matter poor in nitrogen, and less than 200 milligrammes of a matter rich in nitrogen.

\* The mixture must be made in an unglazed porcelain mortar, slightly warmed beforehand, and taking care to triturate gently. If these precautions be not observed, there will be a chance of loss, because the matter will then adhere to the sides of the pestle or of the mortar. After having introduced the mixture into the tube in the ordinary way, the mortar must be immediately rinsed with a little of the soda-lime mixture, and the tube is filled up till within 25 millimetres of the orifice; a plug of ignited asbestos is then introduced, the object of which is to prevent a little of the fine powder from being mechanically carried into the muriatic acid, which would render the determination erroneous, in case potash-lime had been employed, on account of the insolubility of potash-chloride of platinum.

\* The two tubes being connected by a good cork, and the apparatus being disposed as represented (page 767), the process is carried as for the analysis of an organic substance. The ammonia is gradually expelled. According to the composition of the matter, there is at the same time a disengagement of hydrogen and of carburetted gases, which not being absorbable by the liquid, indicate how the combustion is proceeding. This combustion should be conducted in such a way that the gas is disengaged without interruption, otherwise the ammonia might be absorbed by the acid with such a rapidity, that the acid penetrating in the combustion-tube would create a loss, and of course render the analysis void.

\* When substances are analysed by this method, for example, mellon and melamine, &c., in which the relative proportions of

the carbon and of the nitrogen are such, that only very little gas of a non-absorbable nature is disengaged, the operation never safe from projections into the combustion-tube, except have added to the matter to be analysed about its own weight of a non-nitrogenised substance, such as sugar. In this manner the disengagement of ammonia is easily conducted without accident, by reason of the non-absorbable gases produced which traverse the liquid and prevent its ascension into the combustion-tube.

\* The tube having been gradually brought to a red heat, the disengagement of gas having completely ceased, what happens when the mixture has become quite white again, the bent point of the tube is broken, and a quantity of atmospheric air sufficient to expel the ammonia is aspirated. It is advisable to aspirate by means of a tube connected with the limb *g*, containing solid potash, in order to retain the acid fumes expelled by the stream of air.

\* It is indispensable that the mixture should have become white again, for by the contact of ammonia, of carbon, and fixed alkalies, cyanurets are produced, which would cause a loss in nitrogen. By heating sufficiently, all the carbon is ultimately burnt.

\* The combustion being finished, the liquid of the bulb is poured in a porcelain capsule, and the bulbs are washed with a mixture of alcohol and of ether, in order to dissolve the carburets which might adhere to the sides; an excess of solution of chloride of platinum is added to the acid liquor, and the whole is evaporated to dryness.

\* The residuum of the evaporation, which evaporation must have been effected slowly, and in a dish covered with blottin paper, to preserve it from dust, is treated by a mixture of 10 volumes of strong alcohol, and of one volume of ether, which dissolves only the excess of chloride of platinum employed.

\* The ammonio-chloride of platinum is then collected upon a dried filter. It is washed with a like mixture of alcohol and of ether until the washing passes colourless or non-acid, or when they no longer leave any residuum by evaporation. The precipitate is then dried at  $100^{\circ}$ , and weighed in a covered crucible or in a tube; from its weight that of the nitrogen is calculated; 177 parts of this gas represent 2787 of ammonia chloride of platinum.

\* This method, which we have been obliged to describe somewhat minutely, on account of its novelty, appears capable of determining with great accuracy the nitrogen of a great number of organic substances; its principal advantage is, that by it the quantity of the nitrogen may be determined in weight, whilst, by the other method, this determination being effected in volumes, requires the use of a graduated jar, of the mercurial trough, of the barometer, thermometer, and also the taking into account the density of the nitrogen, the coefficient of dilatation of gases, &c.; but this advantage is largely compensated by the greatest defect which an analytical method can present as a means of investigation; namely, it is not generally applicable. It cannot serve for the organic substances which contain nitrogen in the state of nitric acid, and probably also in the state of any other oxygenised combination of nitrogen. Now, as it is generally impossible to know in what state nitrogen exists in an organic product, especially before the analysis of that substance, this process is doubtful and insufficient. The progress which has been made in organic chemistry for the last fifteen years is mostly referrible to the discoveries of accurate and simple processes. Had MM. Will and Warrentrap's method only been employed, it would only have fettered scientific investigation, and it is doubtful whether, until it has been improved, any chemist will resort to it as a means of rectifying the results obtained by the other method.

The process by volumes is doubtless attended with difficulties,

but, at the same time, the results which it yields are per accurate within the limits of approximation, easily apprec and, moreover, its application is quite general.

\* These remarks are made independently of the objection M. Reiset to the method of MM. Will and Warrentrap, ' method is, in the opinion of M. Reiset, an erroneous because the nitrogen of the air can produce ammonia when organic matter is decomposed by an alkaline hydrate. The assertion of M. Reiset, which is the result of numerous experiments, is represented by M. Will as quite groundless.]

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\* The analysis of all the organic substances which consist of hydrogen, carbon, oxygen, and sometimes of nitrogen, performed in the manner which has been described before, is trustworthy only when the body operated upon is perfectly pure, and free from foreign substances. But those conditions are in some cases very difficult to meet, especially when the substance cannot be obtained in the crystallised state. If a substance can produce saline combinations with the base, its atomic weight can be easily calculated by converting it into a neutral salt. If the neutral salt produced contains no water, and crystallises, the quantity of the organic substance is found by the loss, and by comparing the known atomic weight of the base, that of the organic substance is easily ascertained.

\* Formerly, it was customary to combine the organic substance with protoxyde of lead, because in a great number of cases, this oxyde forms, with a great number of organic substances, anhydrous salts, in which its quantity is easily determined. The only drawback to the use of this oxyde is, that it produces with most acids multiple combinations, and therefore, it is impossible to know which of these combinations is neutral, moreover the neutral combination is often mixed with other compounds. Oxyde of silver and other bases have not the same



defect, at least to the same extent, owing to which they are generally used in these experiments.

\* According to Berzelius, the salt of lead may be analysed in the following manner:—The salt is dried at 100° cent. in a current of air, which passes through a long tube filled with fused chloride of calcium, as was said (page 636); it is then left to cool at the ordinary temperature, the current of dry air being passed over it all the while; a certain quantity of it is then weighed in a counterpoised watch-glass, strong enough to bear the heat without breaking, or better still, in a small porcelain crucible; it is then immediately heated over the flame of a spirit-lamp, so that the mass may get inflamed at one of the edges, and the heat is then diminished, in order that the combustion may proceed slowly by itself. Unless this precaution be taken, the heat might so increase during the combustion of the salt, that the mass would become bright red, and a little lead might be volatilised. The combustion being terminated, the mass is heated to incipient redness, in order that none of the charcoal should remain unburnt; it is then allowed to cool, and it is weighed. The residuum is a mixture of lead, and of protoxyde of lead. By pouring dilute acetic acid upon it, the oxyde of lead is dissolved, and on adding afterwards more acetic acid, the pulverulent metal agglomerates into a cohesive mass. This mass is well washed with water, and the water is carefully decanted, which is easily done, on account of the high specific gravity of lead; it is then dried in the water-bath, or on the stove, and it is weighed. For each 100 parts of reduced lead, 7.725 parts of oxygen are added to the ignited residuum, which gives the total quantity of protoxyde of lead existing in the salt. The loss in weight is due, in the anhydrous salts, to the organic substance.

\* This experiment, which needs be performed in small quantities only, and which may be repeated several times in succession, gives, when due care is employed, results which are

much more accurate than any other which might be resorted to for determining the quantity of protoxyde of lead in the combination, and it has the advantage of being performed in a short time.

\* Brunner found that the quantity of protoxyde of lead may be obtained more easily and accurately still by mixing, in the watch-glass or in the crucible, the substance which has to be burnt, with two or three times its weight of fine quartzose sand which has been treated by muriatic acid, and then washed with water and dried; weighing this mixture accurately in the watch-glass or in the crucible, roasting it over the spirit-lamp, taking care to stir it with a flat glass rod, and continuing the roasting until the whole is converted into a powder of a pure yellow colour, and until it ceases to emit little sparks when stirred. The loss of weight observed after the cooling of the watch-glass or of the crucible, indicates immediately the quantity of organic substance contained in the mixture. In effect, the mixture of this substance with pulverised quartz equalises the combustion, and renders it stronger; the mass never reaches a bright red heat, it does not cohere nor intumescence, and the empty spaces which are produced by stirring, allow the air to reach each molecule, so that the combustion is thus easily and completely effected. In order to make sure of this, the residuum is treated by acetic acid, and the acetate of lead is entirely removed by washing with water. If nitric acid is now poured upon the quartz, it does not take up any ponderable quantity of lead, provided the combustion has been well executed.

\* If the organic substance is volatile, or if sulphuric acid can easily convert it into a volatile combination, the salt of lead may be examined by treating it with sulphuric acid, igniting the sulphate of lead obtained, and calculating from its quantity that of the protoxyde of lead.

\* If the organic substance has been combined with oxyde of

silver, the analysis of the silver salt is still more simple, for it suffices to take a weighed quantity of it and to put it in a watch-glass, or, better still, in a small porcelain crucible, and to heat it with care, as has been just said, to incipient redness; there remains pure metallic silver.

The operator must bear in mind that certain salts of silver, produced by organic acids, detonate when heated; such should be converted into chloride of silver.

\* An acid organic substance should never be combined with a fixed alkali, nor with an alkaline earth, and the salt thus obtained should not be employed to burn it with peroxyde of copper, even when this salt can be obtained in the crystalline state. The carbonic acid produced by the combustion combines in part with the alkali or with the earth; now, the action of a prolonged heat in the midst of a large excess of oxyde of copper never expels the whole of the carbonic acid from the fixed carbonates, and thus the result obtained respecting the quantity of the carbon is inexact.

\* After having determined the atomic weight of the substance, it is to be burnt by means of oxyde of copper, either alone or which is quite as well, or even better, combined with a base, and preferably with protoxyde of lead or with oxyde of silver; the quantity of the hydrogen and of the carbon is then determined, and lastly, from the loss of weight, that of the oxygen. It is then necessary to examine whether that quantity of the oxygen of the organic substance is a multiple by a whole number of that of the quantity of the oxygen of the base found in the preceding experiment; at any rate it must not differ much from a multiple of the quantity of oxygen in the base. For, as in the salts which organic acids form with the bases, the oxygen of the first must be a multiple by a whole number of that of the bases, so must the same ratio exist in the combinations of organic substances with the bases; if this is not the case, either some error has crept into the analysis, or else the substance operated upon was not pure.

\*The number of atoms of hydrogen, of carbon, and oxygen, in the substance experimented upon is then calculated. The atoms of the hydrogen are deduced from comparison between the oxygen of the substance and that the base with which it forms a neutral combination. If there be one atom of oxygen in the latter, the organic substance contains as many times more atoms of oxygen as the quantity of that substance is a multiple of that of the base. The number of atoms of oxygen gives that of the atoms of hydrogen of carbon, and even of nitrogen, if the latter be present, comparing the atomic weights of these elements with that of oxygen.

\*Let us illustrate this by an example:—Berzelius found analysing tartaric acid, that this acid yields, with protoxyde of lead, an anhydrous salt, which being analysed, was found to contain in 100 parts 62·7431 of oxyde, and 37·2569 of acid; the atomic weight of lead is 1394·5, that of the tartaric acid deduced from the proportion  $62\cdot7431 : 37\cdot2569 :: 1394\cdot5 : x$  is 828·05. One gramme of tartrate of lead, containing consequently 0·372569 gramme of tartaric acid, was burnt with oxyde of copper; the result obtained was 0·101 gramme of water, and 0·4975 gramme of carbonic acid. But these quantities of the two bodies contain 0·01122 gramme of hydrogen, and 0·137 gramme of carbon; the quantity of oxygen in this quantity of tartaric acid, deduced from the loss, is therefore 0·223 gramme. The oxygen of 0·627431 gramme of protoxyde of lead is 0·04498 gramme; therefore, that of the acid is a multiple by 5 of that of the base. But if the acid contains 5 atoms of oxygen, it contains also, by comparing its atomic weight with that of the carbon and of the hydrogen, 4 atoms of hydrogen and 4 atoms of carbon. Now, the atomic weight of a substance composed of 5 atoms of oxygen, 4 atoms of hydrogen, and 4 atoms of carbon, is 830·707, which agrees almost with the atomic weight which had been calculated from the analysis of the tartrate of lead.

\* If the organic substance is of a basic nature, and forms crystalline salts with the inorganic acids, its atomic weight is determined in the same manner as for the acid organic substances. If a sulphate is chosen, and if that salt is soluble, the sulphuric acid may be accurately determined by the solution of a baryta-salt, and the atomic weight of the organic base is calculated after having previously ascertained whether or not the salt contained water of crystallisation, and in the first case, its quantity must first be determined.

\* There is, however, another manner of determining the capacity of saturation of the organic bases. Very dry muriatic acid gas is passed over a weighed quantity of the substance, which must likewise be very dry. In order afterwards to remove all the excess of muriatic acid gas, a stream of dry atmospheric air is passed over the combination, by means of the apparatus represented (page 636), until its weight remains uniform. The increase of the weight is due to the muriatic acid absorbed. It often happens, however, that a certain quantity of water escapes from the base; in which case the salt should be dissolved in water, and the muriatic acid is determined as chloride of silver.

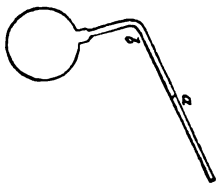
\* With respect to the organic substances which do not form saline combinations with bases nor with acids, the accuracy of the analysis is much more difficult to verify. The operator must rest satisfied with examining whether the proportion of the elements found corresponds to whole atomic numbers of carbon, of hydrogen, of oxygen, and of nitrogen, which, however, may be the case very often, or, at least, very nearly so, for substances which contain a great number of atoms of simple bodies, even though the analysis is not perfectly accurate.

\* When the substances are of a volatile nature, the determination of the specific gravity of their vapour is an excellent means of verifying the accuracy of the analysis.

\* The best is then to employ the method and the apparatus indicated by Dumas. The apparatus and process are both very simple.

\* The process consists in weighing a suitable vessel, preferably a glass globe, provided with a narrow neck, and introducing into it the volatile body, the specific gravity of the vapour which has to be determined, keeping the vessel for some time at a temperature about  $30^{\circ}$  cent. above the boiling point of the volatile body, and fusing afterwards the point of the neck with the blowpipe, the temperature which the base has acquired whilst heated, being observed at the same time. The vessel is again weighed, and its capacity is determined, if this has not been done before the experiment.

\* In order to perform this experiment, take a glass globe of a capacity of about three or four hundred cubic centimetres and solder thereto a narrow glass tube *a*, about eight or ten



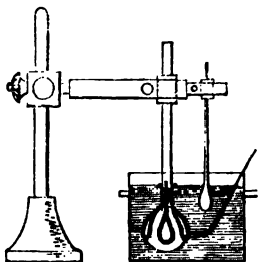
inches long, and about one-twelfth of an inch in diameter, and bend that tube at *b*, after having drawn out its extremity to a fine point. The bulb must be perfectly dry and clean internally; it is carefully weighed, noting at the same time the barometric and thermometric state of the atmosphere.

\* The volatile organic substance must now be introduced into the globe, which is easily done if it is a liquid. The globe is very gently heated, and its point is plunged into the liquid, a certain quantity of which ascends into the globe as it cools. It is not necessary to determine exactly this quantity, it is only requisite that this quantity be more than sufficient to fill completely the capacity of the globe with the vapour of the liquid. Five or six grammes of substance are generally enough.

most cases, when the specific gravity of the vapour is not too considerable.

\* If the organic substance is solid, it must be fused by a gentle heat, and the point of the hot globe is plunged into the liquid. The neck should also be kept hot during the time, in order that the substance may penetrate into the globe.

\* When the substance is much more volatile than water, the glass globe is heated in a water-bath; it is then fastened in the



manner represented by the figure. A good thermometer is plunged in the bath.

\* When the temperature of the water surrounding the globe has attained the boiling point of the organic substance, a stream of its vapour is seen escaping through the point. The temperature of the water is then allowed to rise about 30° centig. above the boiling point of the substance. If the operator observes in the point and in the small portion of the tube out of the water, drops of the substance produced by the condensation of its vapour, they must be removed by holding ignited pieces of charcoal outside of that part of the tube. When no more vapour is seen escaping at the point; for example, when a flame brought near its orifice does not vacillate; the point of the tube is rapidly fused with the blowpipe, whilst the height of the thermometer plunged in the bath is noted. The globe is then immediately withdrawn, it is very carefully dried exteriorly, and after complete cooling it is very accurately

weighed, examining at the same time whether the barometric and thermometric state of the air are the same as when the empty globe was weighed.

\* The vapour of the volatile substance in excess has expelled the atmospheric air of the globe, but, in most cases, not in a complete manner. In order to ascertain how much atmospheric air remains still in bulk, and also what is the bulk of the vapour of the substance, the tube of the globe is plunged into mercury to the point which has been slightly filed is broken under the mercury, and the vacuum produced by the condensation of the vapour, the places where bubbles of air are perceived, are moistened outside with ether, in order to condense the last traces of vapour of the substance. Consequently the portion of the globe which has not been filled by the mercury is to be completely filled with water, and the volume of that water is then measured in a small graduated tube, by which means the volume of the atmospheric air which was not expelled by the vapour of the substance, becomes thus known. The mercury of the globe is now poured into another graduated tube, of a larger size, and from its volume that of the vapour of the substance is determined.

\* The volume of the atmospheric air which remains in the globe is ordinarily from one to three cubic centimetres; sometimes there is none left, and the whole of the capacity of the globe becomes filled with mercury. Sometimes, however, the volume of this air is somewhat considerable, especially when the globe has been heated too long, or not in a uniform manner.

\* If the organic substance is less volatile than water, instead of the water-bath, a liquid of a higher boiling point is employed. For substances the boiling point of which is between  $100^{\circ}$  and  $200^{\circ}$  cent., the best is a bath of chloride of zinc, which was first proposed by Soltmann. This liquid is advantageous, because after the heat has evaporated the water from the concentrated



solution of the salt, the latter gradually begins to decompose without solidifying, if the temperature is augmented.

From the results obtained the specific gravity of the vapour is calculated. The simplest method of doing this is by logarithms, according to a rule expressed by the following formulas, in which all the circumstances have been taken into consideration.

$$\text{Log. } V - \text{Log. } (V - \nu) - \text{Log. } (1 + \delta (\theta - t)) + \text{Log. } (1 + \lambda \theta').$$

$$- \text{Log. } (1 + \lambda t) = \text{Log. } A.$$

$$\text{Log. } A + \text{Log. } P - \text{Log. } V - \text{Log. } s = \text{Log. } B.$$

$$\text{Specific gravity} = A + B.$$

\* The meaning of the letters of the above formulas is as follows:—

$\theta'$  = The high temperature at which the vessel has been soldered.

$t$  = Ordinary temperature at which the weighings have been made.

Both temperatures are expressed in centigrade degrees.

$V$  = Volume of the vessel at temperature  $t$ , expressed in cubic centimetres.

$V - \nu$  = The volume of the vapour, free from air, at the temperature  $t$ , also expressed in cubic centimetres. ( $\nu$  is the volume of atmospheric air mixed with the vapour.)

$\delta$  = The coefficient of the dilatation of the glass, or the increase of bulk, that a mass of glass, which at  $0^\circ$  has the volume 1, (for example, 1 cubic centimetre,) undergoes for each degree centigrade.

$\lambda$  = The same quantity for atmospheric air, and, general, for all gases, according to the determination by Rudberg,  $= 0.00365$ .

$1 + \lambda t'$  = The volume of a mass of air at the temperature  $t'$ , the volume of which at  $0^\circ = 1$ .

$1 + \lambda t$  = The volume of a mass of air at the temperature  $t$ , the volume of which at  $0^\circ = 1$ .

$1 + \delta (t' - t)$  = The volume of a mass of glass at the temperature  $t'$ , the volume of which at  $t^\circ = 1$ , or, what nearly the same thing, at  $0^\circ = 1$ .

$P$  = The increase of weight of the globe full of vapour compared to the globe full of atmospheric air in grammes.

$s$  = The weight of a cubic centimetre of atmospheric air at the temperature  $t$ , and at the barometrical height  $b$ , during the experiment, also grammes.

\* The deduction of the preceding formulas will be found in the *Annals of Poggendorf*, to which the reader is referred.<sup>1</sup> The following example, in which the residuum of atmospheric air is considerable, will serve as a practical illustration :

Let us suppose the results of an experiment to be,

$$\begin{array}{rcl} V = 272.00 \text{ cent. cub.} & t' = 198^\circ.7 \text{ C.} & \\ v = 20.85 & t = 21.2 & \\ \hline V - v = 251.15 & t' - t = 177.5 & \\ P = 0.541 \text{ gram.} & b = 756.8 \text{ millim. at } 0^\circ. & \end{array}$$

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<sup>1</sup> Poggendorf *Annalen*, bd. xli., s. 449.

The calculation is as follows :—

$$\begin{array}{rcl}
 \text{Log. } V & = & 2.43457 \\
 - \text{Log. } (V - v) & = & 2.39993 \\
 \hline
 & & 0.03464 \\
 - \text{Log. } (1 + \delta (t' - t)) & = & 0.00208 \\
 \hline
 & & 0.03256 \\
 + \text{Log. } (1 + \lambda t') & = & 0.23685 \\
 \hline
 & & 0.26941 \\
 - \text{Log. } (1 + \lambda t) & = & 0.03236 \\
 \hline
 & & 0.23705 \dots \text{Number } 1.726 \\
 + \text{Log. } P & = & 0.73320 - 1 \\
 \hline
 & & 0.97025 - 1 \\
 - \text{Log. } V & = & 2.43457 \\
 \hline
 & & 0.53568 - 3 \\
 - \text{Log. } s & = & 0.07934 - 3 \\
 \hline
 & & 0.45634 \dots \text{Number } 2.860 \\
 \hline
 & & \text{Specific gravity} = 4.586
 \end{array}$$

\* In order to obtain easily the weight of a cubic centimetre of the vapour at  $0^\circ$  and at  $760^{\text{mm}}.00$  barometric height, add to the logarithm of the specific gravity found above the logarithm of the weight of a cubic centimetre of dry air at  $0^\circ$  and at  $760^{\text{mm}}.00$ , and look in the tables for the number corresponding to the sum of these two logarithms. Let us express the latter weight by  $8^\circ$ , the above example would give,

$$\begin{array}{rcl}
 \text{Log. } 4.586 & = & 0.66143 \\
 + \text{Log. } 8^\circ & = & 0.11363 - 3 \\
 \hline
 & & 0.77506 - 3 \dots \text{Number } 0.005957 \text{ gramme.}
 \end{array}$$

Therefore a cubic centimetre of the vapour examined weighs  $0.005957$  at  $0^\circ$  and  $760^{\text{mm}}.00$ .

\* In the preceding example the atmospheric air mixed with the vapour has been taken into account, because its volume was considerable, since it was 7 or 8 per cent. of the gaseous mixture, but when it amounts only to one-third or one-half per cent., it may be neglected; neither is it necessary in that

case to take the dilatation of the glass into account; nay, the result obtained without it is more accurate.

\* Let us illustrate this by the calculation of the specific gravity of the vapour of the same liquid alluded to in the preceding example, but assuming that the volume of the atmospheric air amounts only to 1·2 cubic centimetres in 314 hundredths of vapour of liquid. Let us suppose, therefore,

$$\begin{aligned} V &= 315\cdot2 \text{ cub. cent.} & t' &= 197\cdot5 \text{ C.} \\ P &= 0\cdot7105 \text{ gr.} & t &= 22\cdot1 \\ b &= 758\cdot1 \text{ mill. at } 0^\circ t' - t = 175\cdot4 \end{aligned}$$

The calculation is as follows:—

$$\begin{array}{rcl} \text{Log. } (1 + \lambda t') & = & 0\cdot23575 \\ - \text{Log. } (1 + \lambda t) & = & 0\cdot03369 \\ \hline & & 0\cdot20206 \dots \text{Number } 1\cdot593 \\ + \text{Log. } P & = & 0\cdot85156 - 1 \\ \hline & & 0\cdot05362 - 1 \\ - \text{Log. } V - & = & 2\cdot49859 \\ \hline & & 0\cdot55503 - 3 \\ - \text{Log. } s & = & 0\cdot07886 - 3 \\ \hline & & 0\cdot47617 \dots \text{Number } 2\cdot993 \\ \hline \text{Specific gravity} & = & 4\cdot585 \end{array}$$

\* The weight of a cubic centimetre of the vapour is calculated in this case as in the preceding one.

\* The above calculations are much facilitated by tables containing the calculated numbers of  $\log. (1 + \lambda t)$   $\log. (1 + \delta(t' - t))$ , and  $\log. s$  for different temperatures. There remains only to take in the ordinary logarithmic tables, the numbers of  $\log. V$  ( $\log. V - \nu$ ) and  $\log. P$ .

Poggendorf has calculated tables of this kind, which I have reproduced here, on account of their great usefulness.

TABLE I.—*Dilatation of Gases in Centigrade Degrees.*

$$\lambda = 0,00465.$$

t.	Log. (1 + $\lambda$ t).	Difference.	t.	Log. (1 + $\lambda$ t).	Difference.	t.	Log. (1 + $\lambda$ t)	Difference.
0	0,00000		40	0,05918	138	80	0,11126	123
1	0,00158	158	41	0,06056	138	81	0,11249	123
2	0,00316	158	42	0,06194	138	82	0,11371	122
3	0,00473	157	43	0,06331	137	83	0,11493	122
4	0,00629	156	44	0,06468	137	84	0,11614	121
5	0,00785	156	45	0,06605	137	85	0,11735	121
6	0,00941	156	46	0,06741	136	86	0,11856	121
7	0,01096	155	47	0,06876	135	87	0,11977	121
8	0,01250	154	48	0,07011	135	88	0,12097	120
9	0,01404	154	49	0,07146	135	89	0,12217	120
10	0,01557	153	50	0,07280	134	90	0,12336	119
11	0,01710	153	51	0,07414	134	91	0,12455	119
12	0,01862	152	52	0,07547	133	92	0,12574	119
13	0,02013	151	53	0,07680	133	93	0,12693	119
14	0,02164	151	54	0,07813	133	94	0,12811	118
15	0,02315	151	55	0,07945	132	95	0,12929	118
16	0,02465	150	56	0,08077	132	96	0,13046	117
17	0,02615	150	57	0,08209	132	97	0,13163	117
18	0,02764	149	58	0,08340	131	98	0,13280	117
19	0,02912	148	59	0,08470	130	99	0,13397	117
20	0,03060	148	60	0,08600	130	100	0,13513	116
21	0,03207	147	61	0,08730	130	101	0,13629	116
22	0,03354	147	62	0,08860	130	102	0,13745	116
23	0,03501	147	63	0,08989	129	103	0,13860	115
24	0,03647	146	64	0,09117	128	104	0,13975	115
25	0,03792	145	65	0,09246	129	105	0,14090	115
26	0,03937	145	66	0,09374	128	106	0,14205	115
27	0,04082	145	67	0,09501	127	107	0,14319	114
28	0,04226	144	68	0,09628	127	108	0,14433	114
29	0,04370	144	69	0,09755	127	109	0,14546	113
30	0,04513	143	70	0,09882	127	110	0,14659	113
31	0,04655	142	71	0,10008	126	111	0,14772	113
32	0,04798	143	72	0,10133	125	112	0,14885	113
33	0,04939	141	73	0,10259	126	113	0,14997	112
34	0,05080	141	74	0,10384	125	114	0,15109	112
35	0,05222	142	75	0,10508	124	115	0,15221	112
36	0,05362	140	76	0,10633	125	116	0,15333	112
37	0,05502	140	77	0,10757	124	117	0,15444	111
38	0,05641	139	78	0,10880	123	118	0,15555	111
39	0,05780	139	79	0,11003	123	119	0,15666	111

t.	Log. (t + $\lambda$ t).	Difference.	t.	Log. (t + $\lambda$ t).	Difference.	t.	Log. t + $\lambda$ t).
120	0,15776	110	170	0,20965	98	220	0,25600
121	0,15886	110	171	0,21063	98	221	0,25687
122	0,15996	110	172	0,21160	97	222	0,25775
123	0,16105	109	173	0,21257	97	223	0,25863
124	0,16215	110	174	0,21354	97	224	0,25950
125	0,16324	109	175	0,21451	97	225	0,26037
126	0,16432	108	176	0,21548	97	226	0,26124
127	0,16541	109	177	0,21644	96	227	0,26211
128	0,16649	108	178	0,21740	96	228	0,26297
129	0,16757	108	179	0,21836	96	229	0,26384
130	0,16864	107	180	0,21932	96	230	0,26470
131	0,16972	108	181	0,22028	96	231	0,26556
132	0,17079	107	182	0,22123	95	232	0,26642
133	0,17186	107	183	0,22218	95	233	0,26727
134	0,17292	106	184	0,22313	95	234	0,26813
135	0,17399	107	185	0,22408	95	235	0,26899
136	0,17505	106	186	0,22502	94	236	0,26984
137	0,17611	106	187	0,22597	95	237	0,27069
138	0,17716	105	188	0,22691	94	238	0,27154
139	0,17821	105	189	0,22785	94	239	0,27239
140	0,17926	105	190	0,22879	94	240	0,27323
141	0,18031	105	191	0,22972	93	241	0,27408
142	0,18136	105	192	0,23065	93	242	0,27492
143	0,18240	104	193	0,23158	93	243	0,27576
144	0,18344	104	194	0,23251	93	244	0,27660
145	0,18448	104	195	0,23344	93	245	0,27744
146	0,18551	103	196	0,23437	93	246	0,27827
147	0,18655	104	197	0,23529	92	247	0,27911
148	0,18758	103	198	0,23621	92	248	0,27994
149	0,18861	103	199	0,23713	92	249	0,28077
150	0,18963	102	200	0,23805	92	250	0,28160
151	0,19065	102	201	0,23896	91	251	0,28243
152	0,19167	102	202	0,23987	91	252	0,28326
153	0,19269	102	203	0,24079	92	253	0,28408
154	0,19371	102	204	0,24170	91	254	0,28490
155	0,19472	101	205	0,24260	90	255	0,28573
156	0,19573	101	206	0,24351	91	256	0,28655
157	0,19674	101	207	0,24441	90	257	0,28737
158	0,19775	101	208	0,24532	91	258	0,28818
159	0,19875	100	209	0,24622	90	259	0,28900
160	0,19975	100	210	0,24711	89	260	0,28981
161	0,20075	100	211	0,24801	90	261	0,29062
162	0,20175	100	212	0,24890	89	262	0,29144
163	0,20275	100	213	0,24980	90	263	0,29225
164	0,20374	99	214	0,25069	89	264	0,29305
165	0,20473	99	215	0,25158	89	265	0,29386
166	0,20572	99	216	0,25246	88	266	0,29466
167	0,20670	98	217	0,25335	89	267	0,29547
168	0,20769	99	218	0,25423	88	268	0,29627
169	0,20867	98	219	0,25512	89	269	0,29707

t.	Log. (1 - λ t).	Difference.	t.	Log. (1 - λ t).	Difference.	t.	Log. (1 - λ t).	Difference.
270	0,29787	80	280	0,30578	78	290	0,31355	77
271	0,29867	80	281	0,30656	78	291	0,31432	77
272	0,29946	79	282	0,30735	79	292	0,31590	77
273	0,30026	80	283	0,30813	78	293	0,31586	77
274	0,30105	79	284	0,30891	78	294	0,31662	76
275	0,30184	79	285	0,30968	77	295	0,31738	76
276	0,30263	79	286	0,31046	78	296	0,31815	77
277	0,30342	79	287	0,31123	77	297	0,31891	76
278	0,30421	79	288	0,31201	78	298	0,31967	76
279	0,30500	79	289	0,31278	77	299	0,32043	76

TABLE II.—*Dilatation of Gases.*

$$\delta = \frac{1}{37000}.$$

t' - t C°.	Log. (1 + δ (t' - t)).	Difference.	t' - t C°.	Log. (1 + δ (t' - t)).	Difference.
100°	0,00117		200°	0,00234	12
110	0,00129	12	210	0,00246	12
120	0,00140	11	220	0,00257	11
130	0,00152	12	230	0,00269	12
140	0,00164	12	240	0,00281	12
150	0,00176	12	250	0,00293	12
160	0,00187	11	260	0,00304	11
170	0,00199	12	270	0,00316	12
180	0,00211	12	280	0,00328	12
190	0,00222	11	290	0,00339	11

TABLE III.—*Weight of a Cubic Centimetre of Air in Grammes.*

$$= s.$$

t C°.	Log. s b - 760mm, 0.	Difference.	t C°.	Log. s b - 760mm, 0.	Difference.
0	0,11363—3		15	0,09048—3	151
1	0,11205—3	158	16	0,08898—3	150
2	0,11048—3	157	17	0,08749—3	149
3	0,10890—3	158	18	0,08600—3	149
4	0,10734—3	156	19	0,08451—3	149
5	0,10578—3	156	20	0,08303—3	148
6	0,10423—3	155	21	0,08156—3	147
7	0,10268—3	155	22	0,08009—3	147
8	0,10113—3	155	23	0,07863—3	146
9	0,09960—3	153	24	0,07717—3	146
10	0,09807—3	153	25	0,07571—3	146
11	0,09654—3	153	26	0,07426—3	145
12	0,09502—3	152	27	0,07281—3	145
13	0,09350—3	152	28	0,07137—3	144
14	0,09199—3	151	29	0,06994—3	143

TABLE IV.—*Correction of the Logarithms of Table III., which is to say, the Barometer, is above or below 760 mm. during the weighing.*

Millimetre.	Above 760 <sup>mm</sup> , additive. Below 760 <sup>mm</sup> , subtractive.	Millimetre.	Above 760 <sup>mm</sup> , additive. Below 760 <sup>mm</sup> , subtractive.	Millimetre.	Above 760 <sup>mm</sup> , additive. Below 760 <sup>mm</sup> , subtractive.
1	0,00057	4	0,00228	7	0,00399
2	0,00114	5	0,00285	8	0,00456
3	0,00171	6	0,00342	9	0,00513

\* For tenths or hundredths of millimetres, the decimal point is advanced one or two places respectively to the right.

\* We have said before, that the weighing of the vapour substance was a means of verifying the accuracy of the analysis of that substance; we shall show now how this result may be attained.

\* The atomic weights of bodies are, as is known, exactly as the specific weight of their vapours, compared to the specific weight of oxygen, taken as the unit, or as their multiples, or sub-multiples of these weights. Thus, when atomic weights are multiplied by 1.1026, which is the specific gravity of oxygen gas, atmospheric air being 1, the specific weights of the vapour of the bodies obtained, compared to the same standard, are either precisely the same, or else their multiples or sub-multiples of that unit. This is true of all bodies, whether simple or compound. Thus, if the atomic weight of iodine is = 7.89, taking that of oxygen as 1, and the specific gravity of its vapour =  $7.89 \times 1.1026 = 8.70$ , which agrees with the experiment which gave 8.72, the atomic weight of water (oxygen being 1) is = 1.1248, and that of its vapour should according to this rule,  $1.1248 \times 1.1026 = 1.240$ , which is nearly double the number 0.623 obtained by experiment.

\* It is only by experiment that one can ascertain, when



the specific gravities calculated coincide with those which have been really observed, as is the case with iodine, or whether they agree with the latter only, after having been multiplied or divided by a simple number, as is the case with vapour of water. We know, however, from the facts, which have been hitherto observed, that the number by which the calculated specific gravity must be multiplied or divided, is a whole or fractional number, but always a very simple one. When, therefore, we deduce the specific gravity of a vapour directly from the atomic weight, that is to say, when the substance being simple, we multiply its atomic weight by 1.1026, or if it is a compound substance, when we multiply the atomic weights of the respective elements by the number of atoms, and by 1.1026, and then add the products, the specific gravity so calculated must, on being compared with that observed, be either the same as the latter, or in a simple ratio. If this is the case, we may consider that the analysis, or the weighing, is accurate.

The ratio between the calculated specific gravity, and that which has been found shows, whether the gas has experienced a condensation, or a dilatation. Condensation has taken place, if the result found is greater than that calculated; in the contrary case, dilatation has been produced.

\*The finding of the proportion of the condensation, or of the dilatation, may be considered as being the result sought for in weighing vapours; for, when this proportion becomes known, the operator may, from the atomic weight of the substance, or if it is a compound body, from the number and atomic weight of its elements, calculate the specific gravity of the vapour with incomparably more accuracy than it is possible to determine it by weighing.

A few examples will illustrate this clearly.

\* Let us first take a simple substance. The specific gravity of the vapour of sulphur is from 6.51 to 6.617, according to Dumas, and 6.9 according to Mitscherlich; calculated from the atomic weight, it is  $2.0116 \times 1.1026 = 2.2181$ , which is a number three times smaller than that found. If we assume the real

weight to be exactly three times that indicated by calculation that is to say, that at equal volumes the vapour of sulphur contains three times as many atoms as oxygen gas, the weight will be  $2.2181 \times 3 = 6.6543$ .

\* Oxalic ether will now be taken as an example of compound substances. According to Dumas' analysis, this substance is composed of 1 atom of ether =  $C_4 H_{10} O$ , and 1 atom of oxalic acid =  $C_2 O_3$ . In order to calculate the specific gravity of vapour we have thus, according to experiment, that of oxygen gas = 1.1026, and that of hydrogen = 0.0688; that of the vapour of carbon must be deduced from its atomic weight, because carbon could never yet be obtained in the state of vapour, assuming that it corresponds exactly to that weight, it is  $0.76437 \times 1.1026 = 0.8428$ . We have, therefore,

$$\begin{array}{lcl}
 \text{1 atom of ether} & \left\{ \begin{array}{l} 4 \text{ C} = 4 \times 0.8428 = 3.3712 \\ 10 \text{ H} = 10 \times 0.0688 = 0.6880 \\ 1 \text{ O} = 1 \times 1.1026 = 1.1026 \end{array} \right. & \\
 \text{1 atom of oxalic acid} & \left\{ \begin{array}{l} 2 \text{ C} = 2 \times 0.8428 = 1.6856 \\ 3 \text{ O} = 3 \times 1.1026 = 3.3078 \end{array} \right\} & 4.9934 \\
 \text{Calculated specific gravity} & & 10.1552
 \end{array}$$

\* That which was found by Dumas = 5.087. As this number is very nearly half that given by calculation, the inference is, 1st. That the analysis was accurate; 2nd. That the true specific gravity is exactly half that which was calculated, that is to say,  $10.1552 \div 2 = 5.0776$ ; that, consequently, one volume of oxalic ether contains  $\frac{1}{2}$  atom of oxalic ether, or 3 atoms of carbon, 5 of hydrogen and 2 of oxygen. One might also determine how many volumes of ether and of oxalic acid are contained in a volume of oxalic ether but it would be necessary to ascribe a hypothetical specific gravity to oxalic acid, which has not yet been determined in the form of vapour. The calculated specific gravity of the vapour of oxalic acid namely 5.1618 is double that found by experiment; if this should be assumed to be the case with that of the vapour of oxalic ether, that is to say, if it is assumed to be  $4.9934 \times \frac{1}{2} = 2.4967$

one volume of vapour of ether, and one volume of vapour of oxalic acid, would have condensed into one volume of vapour of oxalic ether. But in as much as this condensation is quite hypothetical, so is the number of the volumes of vapour of carbon admitted in the vapour of oxalic ether. Instead of 3 volumes of vapour of carbon, which were admitted formerly in one volume of oxalic ether, there might be 6, for example, if it could be demonstrated that its specific gravity is not 0.8428, but  $\frac{1}{2} \times 0.8428 = 0.4214$ , as is in fact admitted by the French chemists.

## TABLES

FOR CALCULATING THE QUANTITY OF A SUBSTANCE FROM THAT  
WHICH HAS BEEN FOUND OF ANOTHER SUBSTANCE.

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\* IN analysing a substance it is rare to isolate its constituents and to determine their quantity by immediate weighing. The constituents are more generally obtained combined with other substances, for example, sulphur and sulphuric acid in the case of sulphate of baryta. It often happens also, that a combination which forms a constituent part of the decomposed substance, for example an oxide, is converted by the analytic process into another combination, for example, into a chloride, or sulphuret, which is separated instead. Lastly, in certain cases for the sake of greater accuracy, it is preferable to determine the mediate constituent of a substance, instead of its immediate principles, for example, mercury instead of protoxyde of mercury.

\* In all these cases and others of a similar nature, determination of the immediate constituents of the analysed substance is calculated from the simple or from the compound bodies obtained by the analysis.

\* The following tables are intended to facilitate as much as possible these calculations.

\* The first column of the tables under the title FOR gives the names of the substances which are obtained in the course of analytical research, and the quantities of which are to be determined for immediate weighings. The chemical formulae

employed by Berzelius to express, in symbols, the chemical composition of those bodies, has been annexed, in order to prevent the mistakes or doubts which the names alone might create respecting their composition. The explanation of these formulas is found in the *Traité de Chimie* of Berzelius, vol. iv. page 609.

\* The second column, under the title **REQUIRED**, indicates the names of the substances, the quantity of which must be calculated from the weight of the substances mentioned in the first column. The chemical formulas have been annexed there also.

\* The third column (No. 1) indicates the quantity of the substance (required) mentioned in the second column, that 1·00000 part of any weight of the substance (found) mentioned in the first column, contains, or which corresponds to 1·00000 part of the latter. By advancing the decimal point to the right we learn what quantity of substance *required* exists in 10, 100, 1000, &c. parts of the substance *found*.

\* The eight following columns, numbered 2, 3, 4, 5, 6, 7, 8, and 9, mark the quantities of substances *required* which are contained in 2·00000, 3·00000, 4·00000, 5·00000, 6·00000, 7·00000, 8·00000, and 9·00000 parts of any weight of substance *found*, mentioned in the first column, or corresponding to these numbers of parts.

\* Now it is easy, by means of a simple addition, to find the quantity of substance *required* from any number of a unit of weight of substances *found*. To do this, for every figure of the quantity, in weight of the substance *found*, the operator adds together the numbers marked on the lines corresponding to the substances *required*, the last nine columns of the tables numbered 1, 2, 3, 4, 5, 6, 7, 8, and 9. As, however, the numbers of the substance required, mentioned in the nine columns of figures correspond to 1·00000, 2·00000, &c. parts of the substance found, it is necessary, in order to find the quantity which corresponds to 0·1, 0·01, 0·001, &c., part of the substance *found*, to advance the decimal point one, two, three places to the left.

In the same manner it is advanced to the right, for the purpose of determining the quantity which corresponds to 10, 100, 1 &c., parts of the substance *found*.

\* For example: required how much potash is contained 2.658 grammes of sulphate of potash—look for sulphate of potash in Tab. XXXV. (POTASSIUM), and add together following numbers :

From column 2	(without altering the place of the decimal point) . . . . .	1.08134
From column 6	(advancing the decimal point one place to the left) . . . . .	0.32440
From column 5	(advancing the decimal point two places to the left) . . . . .	0.02703
From column 8	(advancing the decimal point three places to the left . . . . .	0.00432

2.658 grammes of sulphate of potash contain 1.43709 grms. of potash

\* It is immediately seen that, in almost all calculations, last figures of the numbers which have to be added together may be neglected without grave error.

\* This disposition of the tables, which Poggendorf was first to employ, spares to those who are not accustomed to use of logarithmic tables, a multitude of troublesome multiplications, and divisions. But even those who are accustomed to logarithmic calculations, will find these tables more convenient for the calculations required in chemical analyses. Last they yield results much more accurate than those of logarithmic tables, or scales of equivalents, which should never be used by any chemist in cases of rigorous analysis.

\* The numbers contained in the tables have been calculated from the atomic weights of the simple bodies admitted by Berzelius, and which were deduced from experiments made by himself. They have been partly determined from new numbers admitted by Berzelius. With each simple body, the weight of its atom has been given, in order that any one may be enabled to verify the accuracy of the numbers indicated in the tables.

\* The tables contain, among the substances from the quantity of which that of other substances may be calculated, only those which are mentioned in the course of this work, except for CHLORINE and SULPHUR (Tabs. XII. and XLII.), where the quantity of the chlorine, and of the sulphur of all the metallic chlorides and sulphurets, have been given. In the same manner, in all the combinations of the various simple bodies with oxygen, the quantity of the oxygen, and that of the simple body, has been given.

\* It is easy, however, from the substances which are not mentioned in the tables, but the atomic composition of which is known, to calculate the quantity of other substances, or rather to determine how much of these corresponds to those. I shall only give here a few examples, in order to illustrate this proposition.

\* Required, for example, how much perchloride of copper would be yielded by a given quantity of protoxyde of copper (*oxyde cuivrique*) by dissolving the latter in muriatic acid, and evaporating the solution to perfect dryness. As this determination is scarcely wanted in quantitative analysis, we have not, in Tab. XV. (Article, Protoxyde of Copper—*Oxyde Cuivrique*), mentioned what is the quantity of protochloride of copper (*chlorure cuivrique*), corresponding to a given quantity of this oxyde. Nothing is, however, more easily calculated; let us suppose that the quantity of protoxyde of copper (*oxyde cuivrique*) is 1.359 grammes. According to the third and fourth lines of Tab. XV., that quantity contains 1.085 gramme of copper, and 0.274 gramme of oxygen. The seventh line of Tab. XII. shows how much chlorine corresponds to 0.274 gramme of oxygen, that is to say, 1.213 gramme. If this quantity be added to that of 1.085 gramme of copper, the result is 2.298 gramme of protochloride of copper (*chlorure cuivrique*).

\* If, on the contrary, the question is how much protoxyde of copper (*oxyde cuivrique*) would be produced by a given quantity, for example, 2.298 of protochloride of copper (*chlorure cuivrique*),

if this chloride were dissolved in water, and decomposed by a solution of potash, the thirty-seventh series of Tables shows how much chlorine 2.298 gramme of proto-chloride of copper (*chlorure cuivrique*) contains, and it is found that it contains 1.213 of chlorine, and consequently, also 1.085 of copper. The eighth series of Tab. XII. shows that 0.274 gramme of chlorine corresponds to 0.274 gramme of oxygen. If the latter quantity be added with 1.085 gramme of copper, the result is 1.359 gramme of protoxyde of copper (*oxyde cuivrique*), corresponding to 2.298 gramme of protochloride of copper (*chlorure cuivrique*).

\* In certain cases of a more complicated nature, notes have been appended at the end of some tables, which notes refer to passages in the text of the work. Other problems will be solved by the intelligent reader, the solution of which can be immediately obtained by the tables.



## ATOMIC WEIGHTS OF SIMPLE BODIES.

Simple Bodies.	Symbols.	Equivalents. Oxygen, O = 100.	Simple Bodies.	Symbols.	Equivalents. Oxygen, O = 100.
I. Aluminium . .	Al <sup>3</sup>	171,167	XXVIII. Molybdenum . .	Mo	598,525
II. Antimony . .	As <sup>3</sup>	342,334		Mo <sup>2</sup>	1197,050
	Sb	806,452	XXIX. Nickel . .	Ni	369,675
	Sb <sup>2</sup>	1612,904		Ni <sup>2</sup>	739,350
III. Arsenic . .	As	470,042	XXX. Nitrogen . .	N	88,518
	As <sup>2</sup>	940,084		N <sup>2</sup>	177,036
IV. Barium . .	Ba	856,880	XXXI. Osmium . .	Os	1244,210
	Ba <sup>2</sup>	1713,760		Os <sup>2</sup>	2488,420
V. Bismuth . .	Bi	886,918	XXXII. Palladium . .	Pd	665,840
	Bi <sup>2</sup>	1773,836		Pd <sup>2</sup>	1331,680
VI. Boron . .	B	135,983	XXXIII. Phosphorus . .	P	196,155
	B <sup>2</sup>	271,966		P <sup>2</sup>	392,310
VII. Bromine . .	Br	489,150	XXXIV. Platinum . .	Pt	1233,260
	Br <sup>2</sup>	978,300		Pt <sup>2</sup>	2466,520
VIII. Cadmium . .	Cd	696,767	XXXV. Potassium . .	K	489,916
	Cd <sup>2</sup>	1393,534		K <sup>2</sup>	979,832
IX. Calcium . .	Ca	256,019	XXXVI. Rhodium . .	R	651,400
	Ca <sup>2</sup>	512,038		R <sup>2</sup>	1302,800
X. Carbon . .	C	76,437	XXXVII. Selenium . .	Se	494,582
	C <sup>2</sup>	152,875		Se <sup>2</sup>	989,164
XI. Cerium . .	Ce	574,718	XXXVIII. Silicium . .	Si	277,478
	Ce <sup>2</sup>	1149,436		Si <sup>2</sup>	554,956
XII. Chlorine . .	Cl	221,325	XXXIX. Silver . .	Ag	1351,607
	Cl <sup>2</sup>	442,650		Ag <sup>2</sup>	2703,214
XIII. Chromium . .	Cr	351,819		Na	290,897
	Cr <sup>2</sup>	703,638	XL. Sodium . .	Na <sup>2</sup>	581,794
XIV. Cobalt . .	Co	368,991		Sr	547,285
	Co <sup>2</sup>	737,982	XLI. Strontium . .	Sr <sup>2</sup>	1094,570
XV. Copper . .	Cu	395,695		S	201,165
	Cu <sup>2</sup>	791,390	XLII. Sulphur . .	S <sup>2</sup>	402,330
XVI. Fluorine . .	F	116,900	XLIII. Tantalum . .	Ta	1153,715
	F <sup>2</sup>	233,800		Ta <sup>2</sup>	2307,430
XVII. Glucinum . .	Be	331,479	XLIV. Tellurium . .	Te	802,121
	Be <sup>2</sup>	662,958		Te <sup>2</sup>	1604,242
XVIII. Gold . .	Au	1243,013	XLV. Thorinium . .	Th	744,900
	Au <sup>2</sup>	2486,026		Th <sup>2</sup>	1489,800
XIX. Hydrogen . .	H	6,2398	XLVI. Tin . .	Sn	735,294
	H <sup>2</sup>	12,4796		Sn <sup>2</sup>	1470,588
XX. Iodine . .	I	789,145	XLVII. Titanium . .	Ti	303,686
	I <sup>2</sup>	1578,290		Ti <sup>2</sup>	607,372
XXI. Iridium . .	Ir	1233,260	XLVIII. Tungsten . .	W	1183,200
	Ir <sup>2</sup>	2466,520		W <sup>2</sup>	2366,400
XXII. Iron . .	Fe	339,213	XLIX. Uranium . .	U	2711,360
	Fe <sup>2</sup>	678,426		U <sup>2</sup>	5422,720
XXIII. Lead . .	Pb	1294,498		V	855,840
	Pb <sup>2</sup>	2588,996	L. Vanadium . .	V <sup>2</sup>	1711,680
XXIV. Lithium . .	L	81,320		Y	401,840
	L <sup>2</sup>	162,640	LI. Yttrium . .	Y <sup>2</sup>	803,680
XXV. Magnesium . .	Mg	158,353		Zn	403,226
	Mg <sup>2</sup>	316,706	LII. Zinc . .	Zn <sup>2</sup>	806,452
XXVI. Manganese . .	Mn	345,900	LIII. Zirconium . .	Zr	420,238
	Mn <sup>2</sup>	691,800		Zr <sup>2</sup>	840,476
XXVII. Mercury . .	Hg	1265,822			
	Hg <sup>2</sup>	2531,644			



FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
III. ARSENIC, As.										
1. Arsenious Acid As <sup>3</sup> O <sub>5</sub>	Arsenic As <sup>3</sup>	0,75808	1,51616	2,27424	3,03232	3,79040	4,54849	5,30657	6,06465	6,82273
2. Arsenious Acid As <sup>3</sup> O <sub>5</sub>	Oxygen O <sub>5</sub>	0,24192	0,48384	0,72576	0,96768	1,20960	1,45151	1,69343	1,93535	2,17727
3. Arsenic Acid As <sup>5</sup> O <sub>6</sub>	Arsenic As <sup>5</sup>	0,65280	1,30560	1,95839	2,61119	3,26399	3,91679	4,56959	5,22238	5,87518
4. Arsenic Acid As <sup>5</sup> O <sub>6</sub>	Oxygen O <sub>6</sub>	0,34720	0,69440	1,04161	1,38881	1,73601	2,08321	2,43041	2,77762	3,12482
5. Sulphuret of Arsenic As <sup>3</sup> S <sub>2</sub>	Arsenic As <sup>3</sup>	0,60903	1,21806	1,82709	2,43612	3,04515	3,65418	4,26321	4,87224	5,48127
6. Sulphuret of Arsenic As <sup>3</sup> S <sub>2</sub>	Arsenious Acid As <sup>3</sup> O <sub>5</sub>	0,80338	1,60676	2,41014	3,21352	4,01690	4,82028	5,62366	6,42704	7,23042
7. Sulphuret of Arsenic As <sup>3</sup> S <sub>2</sub>	Arsenic As <sup>3</sup>	0,48311	0,96622	1,44933	1,93244	2,41555	2,89866	3,38177	3,86488	4,34799
8. Sulphuret of Arsenic As <sup>3</sup> S <sub>2</sub>	Arsenious Acid As <sup>3</sup> O <sub>5</sub>	0,74006	1,48012	2,22018	2,96024	3,70030	4,44036	5,18042	5,92048	6,66054
9. Arsenic As <sup>5</sup>	Arsenious Acid As <sup>3</sup> O <sub>5</sub>	1,31912	2,63824	3,95736	5,27648	6,59560	7,91472	9,23384	10,55296	11,87208
10. Arsenic As <sup>5</sup>	Arsenious Acid As <sup>3</sup> O <sub>5</sub>	1,53186	3,06372	4,59558	6,12744	7,65930	9,19116	10,72302	12,25488	13,78674
IV. BARIUM, Ba.										
1. Baryta Ba O	Barium Ba	0,89549	1,79099	2,68648	3,48198	4,27747	5,07296	5,86846	6,66395	7,45945
2. Baryta Ba O	Oxygen O	0,10451	0,20901	0,31352	0,41802	0,52253	0,62704	0,73154	0,83605	0,94055
3. Sulphate of Baryta Ba O + SO <sub>3</sub>	Baryta Ba O	0,65628	1,31256	1,96884	2,62512	3,28140	3,93768	4,59396	5,25024	5,90652
4. Carbonate of Baryta Ba O + CO <sub>2</sub>	Baryta Ba O	0,77586	1,55172	2,32758	3,10344	3,87930	4,65516	5,43102	6,20688	6,98274

FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
<b>BARIUM—(Continued).</b>										
5. Chloride of Barium Ba Cl <sub>2</sub> .	Baryta Ba O	0,73633	1,47266	2,20899	2,94532	3,68165	4,41798	5,15431	5,89064	6,62697
6. Chloride of Barium Ba Cl <sub>2</sub> .	Barium Ba	0,65938	1,31876	1,97814	2,63752	3,29690	3,95628	4,61566	5,27504	5,93442
7. Silicifluoride of Barium F <sup>2</sup> <sub>2</sub> Ba <sub>2</sub> + F <sup>2</sup> <sub>2</sub> Si <sub>2</sub> .	Baryta 3 Ba O	0,16297	0,36594	0,54891	0,73188	0,91485	1,09782	1,28079	1,46376	1,64673
8. Nitrate of Baryta Ba + N <sup>2</sup> O <sub>5</sub> .	Baryta Ba O	0,58564	1,17128	1,75692	2,34256	2,92820	3,51384	4,09948	4,68512	5,27076
<b>V. BISMUTH, Bi.</b>										
1. Oxide of Bismuth Bi O	Bismuth Bi	0,89867	1,79735	2,69602	3,59470	4,49337	5,39204	6,29072	7,18939	8,08807
2. Oxide of Bismuth Bi O	Oxygen O	0,10133	0,20265	0,30398	0,40530	0,50663	0,60796	0,70928	0,81061	0,91193
<b>VI. BORON, B.</b>										
1. Boracic Acid B + 3 O	Boron B	0,31190	0,62380	0,93570	1,24760	1,55950	1,87140	2,18330	2,49520	2,80710
2. Boracic Acid B + 3 O	Oxygen O <sub>3</sub>	0,68810	1,37620	2,06430	2,75240	3,44050	4,12860	4,81670	5,50480	6,19290
<b>VII. BROMINE, Br.</b>										
1. Bromic Acid Br <sup>2</sup> O <sub>4</sub>	Bromine Br <sup>2</sup>	0,66177	1,32355	1,98532	2,64710	3,30887	3,97064	4,63242	5,29419	5,95597
2. Bromic Acid Br <sup>2</sup> O <sub>5</sub>	Oxygen O <sub>5</sub>	0,33823	0,67645	1,01468	1,35290	1,69113	2,02936	2,36758	2,70581	3,04403
3. Oxygen O	Bromine Br <sup>2</sup>	9,76200	19,56600	29,34900	39,13200	48,91500	58,69800	68,48100	78,26400	88,04700

FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
<b>BROMINE—(Continued).</b>										
5. Bromide of Silver Ag Br <sup>a</sup> . . . . .	Hydrobromic Acid H <sup>a</sup> Br <sup>a</sup> . . . . .	0,42524	0,86048	1,27572	1,70096	2,12620	2,55144	2,97668	3,40192	3,82716
6. Hydrobromic Acid H <sup>a</sup> Br <sup>a</sup> . . . . .	Bromine Br <sup>a</sup> . . . . .	0,98740	1,97480	2,96220	3,94960	4,93700	5,92440	6,91180	7,89920	8,88660
7. Bromine Br <sup>a</sup> . . . . .	Oxygen O . . . . .	0,10222	0,20444	0,30666	0,40888	0,51110	0,61332	0,71554	0,81776	0,91998
<b>VIII. CADMIUM, Cd.</b>										
1. Oxide of Cadmium Cd O . . . . .	Cadmium Cd . . . . .	0,87449	1,74899	2,62348	3,49797	4,37246	5,24696	6,12145	6,99594	7,87044
2. Oxide of Cadmium Cd O . . . . .	Oxygen O . . . . .	0,12551	0,25101	0,37652	0,50203	0,62754	0,75304	0,87855	1,00406	1,12956
3. Sulphuret of Cadmium Cd S . . . . .	Oxide of Cadmium Cd O . . . . .	0,88734	1,77468	2,66202	3,54936	4,43670	5,32404	6,21138	7,09872	7,98606
<b>IX. CALCIUM, Ca.</b>										
1. Lime Ca O . . . . .	Calcium Ca . . . . .	0,71911	1,43823	2,15735	2,87646	3,59558	4,31470	5,03381	5,75293	6,47204
2. Lime Ca O . . . . .	Oxygen O . . . . .	0,28089	0,56177	0,84265	1,12354	1,40442	1,68530	1,96619	2,24707	2,52796
3. Sulphuret of Calcium Ca O + S O <sub>8</sub> . . . . .	Lime Ca O . . . . .	0,41532	0,83064	1,24596	1,66128	2,07660	2,49192	2,90724	3,32256	3,73788
4. Carbonate of Lime Ca O + C O <sub>2</sub> . . . . .	Lime Ca O . . . . .	0,56292	1,12584	1,68876	2,25168	2,81460	3,37752	3,94044	4,50336	5,06628
<b>X. CARBON, C.</b>										
1. Oxide of Carbon C O . . . . .	Carbon C . . . . .	0,43323	0,86645	1,29968	1,73290	2,16613	2,59936	3,03258	3,46581	3,89903
2. Oxide of Carbon C O . . . . .	Oxygen O . . . . .	0,56677	1,13355	1,70032	2,26710	2,83387	3,40064	3,96742	4,53419	5,10097

FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
<b>CARBON—(Continued).</b>										
3. Oxalic Acid C <sup>2</sup> O <sub>3</sub>	Carbon C <sup>2</sup>	0,33757	0,67514	1,01271	1,35028	1,68785	2,02542	2,36299	2,70056	3,03813
4. Oxalic Acid C <sup>2</sup> O <sub>3</sub>	Oxygen O <sub>3</sub>	0,56243	1,32486	1,98729	2,64972	3,31215	3,97458	4,63701	5,29944	5,96187
5. Carbonic Acid C O <sub>2</sub>	Carbon C	0,27651	0,55302	0,82952	1,10603	1,38254	1,65905	1,93556	2,21206	2,48857
6. Carbonic Acid C O <sub>2</sub>	Oxygen O <sub>2</sub>	0,72349	1,44698	2,17048	2,89397	3,61746	4,34095	5,06444	5,78794	6,51143
7. Carbonic Acid C O <sub>2</sub>	Oxide of Carbon C O	0,63825	1,27650	1,91475	2,55300	3,19125	3,82950	4,46775	5,10600	5,74425
8. Carbonic Acid C O <sub>2</sub>	Oxalic Acid C <sup>2</sup> O <sub>3</sub>	0,81913	1,63826	2,45739	3,27652	4,09565	4,91478	5,73391	6,55304	7,37217
9. Carbonate of Lime Ca O + C O <sub>2</sub>	Oxalic Acid C <sup>2</sup> O <sub>3</sub>	0,35803	0,71606	1,07409	1,43212	1,79015	2,14818	2,50621	2,86424	3,22227
10. Carbonate of Lime Ca O + C O <sub>2</sub>	Carbonic Acid C O <sub>2</sub>	0,43708	0,87416	1,31124	1,74832	2,18540	2,62248	3,05956	3,49664	3,93372
11. Carbonate of Baryta Ba O + C O <sub>2</sub>	Carbonic Acid C O <sub>2</sub>	0,22414	0,44828	0,67242	0,89656	1,12070	1,34484	1,56898	1,79312	2,01726
<b>XI. CERIUM, Ce.</b>										
1. Protoxide of Cerium Ce O	Cerium Ce	0,85179	1,70358	2,55537	3,40716	4,25895	5,11074	5,96253	6,81432	7,66611
2. Protoxide of Cerium Ce O	Oxygen O	0,14821	0,29642	0,44463	0,59284	0,74105	0,88926	1,03747	1,18568	1,33389
3. Sesquioxide of Cerium Ce <sub>2</sub> O <sub>3</sub>	Cerium Ce <sub>2</sub>	0,79302	1,58605	2,37907	3,17209	3,96511	4,75814	5,55116	6,34418	7,13721

FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
XII. CHLORINE, Cl.										
1. Chlorous Acid	Chlorine	0,31572	1,63144	2,44716	3,26288	4,07859	4,89431	5,71003	6,52575	7,34147
Cl <sup>2</sup> O	Cl <sup>2</sup>									
2. Chlorous Acid	Oxygen	0,18428	0,36856	0,55284	0,73712	0,92141	1,10569	1,28997	1,47425	1,65853
Cl <sup>2</sup> O	O									
3. Chloric Acid	Chlorine	0,46658	0,93316	1,40874	1,87932	2,34790	2,81749	3,28707	3,75665	4,22623
Cl <sup>2</sup> O <sub>5</sub>	Cl <sup>2</sup>									
4. Chloric Acid	Oxygen	0,53042	1,06084	1,59126	2,12168	2,65210	3,18251	3,71293	4,24335	4,77377
Cl <sup>2</sup> O <sub>5</sub>	O <sub>5</sub>									
5. Oxochloric Acid	Chlorine	0,38739	0,77478	1,16217	1,54956	1,93694	2,32433	2,71172	3,09911	3,48650
Cl <sup>2</sup> O <sub>7</sub>	Cl <sup>2</sup>									
6. Oxochloric Acid	Oxygen	0,61261	1,22522	1,83783	2,45044	3,06306	3,67567	4,28828	4,90089	5,51350
Cl <sup>2</sup> O <sub>7</sub>	O <sub>7</sub>									
7. Oxygen	Chlorine	4,42650	8,85300	13,27950	17,70600	22,13250	26,55900	30,98550	35,41200	39,83850
O	Cl <sup>2</sup>									
8. Chlorine	Oxygen	0,22591	0,45182	0,67773	0,90364	1,12955	1,35546	1,58137	1,80728	2,03319
Cl <sup>2</sup>	O									
9. Chloride of Potassium	Chlorine	0,47466	0,94932	1,42398	1,89864	2,37330	2,84796	3,32262	3,79728	4,27194
K Cl	Cl <sub>2</sub>									
10. Chloride of Sodium	Chlorine	0,60344	1,20688	1,81032	2,41376	3,01720	3,62064	4,22408	4,82752	5,43096
Na Cl <sub>2</sub>	Cl <sub>2</sub>									
11. Chloride of Lithium	Chlorine	0,34480	1,68960	2,53440	3,37920	4,22400	5,06880	5,91360	6,75840	7,60320
Li Cl <sub>2</sub>	Cl <sub>2</sub>									
12. Chloride of Barium	Chlorine	0,34062	0,68124	1,02186	1,36248	1,70310	2,04372	2,38434	2,72496	3,06558
Ba Cl <sub>2</sub>	Cl <sub>2</sub>									
13. Chloride of Strontium	Chlorine	0,44715	0,89430	1,34145	1,78860	2,23575	2,68290	3,13005	3,57720	4,02435
Sr Cl <sub>2</sub>	Cl <sub>2</sub>									
14. Chloride of Calcium	Chlorine	0,63356	1,26712	1,90068	2,53424	3,16780	3,80136	4,43492	5,06848	5,70204
Ca Cl <sub>2</sub>	Cl <sub>2</sub>									
15. Chloride of Magnesium	Chlorine	0,73652	1,47304	2,20956	2,94608	3,68260	4,41912	5,15564	5,89216	6,62868
Mg Cl <sub>2</sub>	Cl <sub>2</sub>									
16. Chloride of Aluminium	Chlorine	0,79504	1,59008	2,38512	3,18016	3,97520	4,77024	5,56528	6,36032	7,15536
Al <sup>3</sup> Cl <sub>3</sub>	Cl <sub>3</sub>									





FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
CHLORINE—(Continued).										
33. Chloride of Bismuth Bi Cl <sub>2</sub>	Chlorine Cl <sub>2</sub>	0,33293	0,66586	0,99879	1,33172	1,66465	1,99758	2,33051	2,66344	2,99637
34. Subchloride of Uranium U Cl <sub>2</sub>	Chlorine Cl <sub>2</sub>	0,14035	0,28070	0,42105	0,56140	0,70175	0,84210	0,98245	1,12280	1,26315
35. Perchloride of Uranium U Cl <sub>3</sub>	Chlorine Cl <sub>2</sub>	0,19671	0,39342	0,59013	0,78684	0,98355	1,18026	1,37697	1,57368	1,77039
36. Subchloride of Copper Cu Cl	Chlorine Cl <sub>2</sub>	0,35870	0,71740	1,07610	1,43480	1,79350	2,15220	2,51090	2,86960	3,22830
37. Protochloride of Copper Cu Cl <sub>2</sub>	Chlorine Cl <sub>2</sub>	0,52801	1,05602	1,58403	2,11204	2,64005	3,16806	3,69607	4,22408	4,75209
38. Chloride of Silver Ag Cl <sub>2</sub>	Chlorine Cl <sub>2</sub>	0,24670	0,49340	0,74010	0,98680	1,23350	1,48020	1,72690	1,97360	2,22030
39. Chloride of Silver Ag Cl <sub>2</sub>	Muriatic Acid Cl <sup>+</sup> H <sup>+</sup>	0,25366	0,50732	0,76098	1,01464	1,26830	1,52196	1,77562	2,02928	2,28294
40. Subchloride of Mercury Hg Cl	Chlorine Cl <sub>2</sub>	0,14883	0,29766	0,44649	0,59532	0,74415	0,89298	1,04181	1,19064	1,33947
41. Perchloride of Mercury Hg Cl <sub>2</sub>	Chlorine Cl <sub>2</sub>	0,25909	0,51818	0,77727	1,03636	1,29545	1,55454	1,81363	2,07272	2,33181
42. Bichloride of Rhodium R Cl <sub>2</sub>	Chlorine Cl <sub>2</sub>	0,40460	0,80920	1,21380	1,61840	2,02300	2,42760	2,83220	3,23680	3,64140
43. Terechloride of Rhodium R Cl <sub>3</sub>	Chlorine Cl <sub>2</sub>	0,50473	1,00956	1,51434	2,01912	2,52390	3,02868	3,53346	4,03824	4,54302
44. Protochloride of Palladium Pd Cl <sub>2</sub>	Chlorine Cl <sub>2</sub>	0,39933	0,79866	1,19799	1,59732	1,99665	2,39598	2,79531	3,19464	3,59397
45. Perchloride of Palladium Pd Cl <sub>3</sub>	Chlorine Cl <sub>2</sub>	0,57074	1,14148	1,71222	2,28296	2,85370	3,42444	3,99518	4,56592	5,13666
46. Protochloride of Iridium Ir Cl <sub>2</sub>	Chlorine Cl <sub>2</sub>	0,26413	0,52826	0,79239	1,05652	1,32065	1,58478	1,84891	2,11304	2,37717
47. Sesquichloride of Iridium Ir <sup>3</sup> Cl <sub>3</sub>	Chlorine Cl <sub>2</sub>	0,34997	0,69994	1,04991	1,39988	1,74985	2,09982	2,44979	2,79976	3,14973
48. Deutochloride of Iridium Ir Cl <sub>4</sub>	Chlorine Cl <sub>2</sub>	0,41788	0,83576	1,25364	1,67152	2,08940	2,50728	2,92516	3,34304	3,76092

FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
CHLORINE—(Continued).										
49. Perchloride of Iridium Ir Cl <sub>6</sub>	Chlorine Cl <sub>6</sub>	0,51849	1,03698	1,55547	2,07396	2,59245	3,11094	3,62943	4,14792	4,66641
50. Protochloride of Osmium Os Cl <sub>2</sub>	Chlorine Cl <sub>2</sub>	0,29241	0,58482	0,87723	1,04964	1,31205	1,57446	1,83687	2,09928	2,36169
51. Sequichloride of Osmium Os Cl <sub>3</sub>	Chlorine Cl <sub>3</sub>	0,34796	0,59592	1,04388	1,39184	1,73980	2,08776	2,43572	2,78368	3,13164
52. Deutochloride of Osmium Os Cl <sub>4</sub>	Chlorine Cl <sub>4</sub>	0,41573	0,83146	1,24719	1,66292	2,07865	2,49438	2,91011	3,32584	3,74157
53. Perchloride of Osmium Os Cl <sub>5</sub>	Chlorine Cl <sub>5</sub>	0,51628	1,03256	1,54884	2,06512	2,58140	3,09768	3,61396	4,13024	4,64652
54. Protochloride of Platinum Pt Cl <sub>2</sub>	Chlorine Cl <sub>2</sub>	0,26413	0,52826	0,79239	1,05652	1,32065	1,58478	1,84891	2,11304	2,37717
55. Perchloride of Platinum Pt Cl <sub>2</sub> <sup>2</sup>	Chlorine Cl <sub>2</sub> <sup>2</sup>	0,41788	0,83576	1,25364	1,67152	2,08940	2,50728	2,92516	3,34304	3,76092
56. Protochloride of Gold Au <sub>2</sub> Cl <sub>2</sub>	Chlorine Cl <sub>2</sub>	0,15114	0,30228	0,45342	0,60456	0,75570	0,90684	1,05798	1,20912	1,36026
57. Perchloride of Gold Au <sub>2</sub> Cl <sub>2</sub> <sup>2</sup>	Chlorine Cl <sub>2</sub> <sup>2</sup>	0,34818	0,69636	1,04454	1,39272	1,74090	2,08908	2,43726	2,78544	3,13362
58. Protochloride of Tin Sn Cl <sub>2</sub>	Chlorine Cl <sub>2</sub>	0,37578	0,75156	1,12734	1,50312	1,87890	2,25468	2,63046	3,00624	3,38202
59. Perchloride of Tin Sn Cl <sub>4</sub>	Chlorine Cl <sub>4</sub>	0,54628	1,09256	1,63884	2,18512	2,73140	3,27768	3,82396	4,37024	4,91652
60. Bichloride of Titanium Ti Cl <sub>2</sub>	Chlorine Cl <sub>2</sub>	0,74458	1,48916	2,23374	2,97832	3,72290	4,46748	5,21206	5,95664	6,70122
61. Sequichloride of Antimony Sb <sub>2</sub> Cl <sub>3</sub>	Chlorine Cl <sub>3</sub>	0,45155	0,90310	1,35465	1,80620	2,25775	2,70930	3,16085	3,61240	4,06395
62. Perchloride of Antimony Sb <sub>2</sub> Cl <sub>5</sub>	Chlorine Cl <sub>5</sub>	0,57845	1,15690	1,73535	2,31380	2,89225	3,47070	4,04915	4,62760	5,20605
63. Chloride of Tungsten W Cl <sub>2</sub>	Chlorine Cl <sub>2</sub>	0,42799	0,85598	1,28397	1,71196	2,13995	2,56794	2,99593	3,42392	3,85191

FOUND.	REQUIRED.	1.	2	3.	4.	5.	6.	7.	8.	9.
<b>CHLORINE—(Continued).</b>										
65. Chloride of Molybdenum Mo Cl <sup>2</sup>	Chlorine Cl <sup>2</sup>	0,42515	0,85030	1,27545	1,70060	2,12575	2,55090	2,97605	3,40120	3,82635
66. Perchloride of Molybdenum Mo Cl <sup>2</sup>	Chlorine Cl <sup>2</sup>	0,59664	1,19328	1,78992	2,38656	2,98320	3,57984	4,17648	4,77312	5,36976
67. Perchloride of Molybdenum Mo Cl <sup>2</sup>	Chlorine Cl <sup>2</sup>	0,68932	1,37864	2,06796	2,75728	3,44660	4,13592	4,82524	5,51456	6,20388
68. Bichloride of Vanadium V Cl <sup>2</sup>	Chlorine Cl <sup>2</sup>	0,50946	1,01892	1,52838	2,03784	2,54730	3,05676	3,56622	4,07568	4,58514
69. Terechloride of Vanadium V Cl <sup>2</sup>	Chlorine Cl <sup>2</sup>	0,60809	1,21618	1,82427	2,43236	3,04045	3,64854	4,25663	4,86472	5,47281
70. Sesquichloride of Chromium Cr <sup>3</sup> Cl <sup>2</sup>	Chlorine Cl <sup>2</sup>	0,65865	1,31730	1,96095	2,61460	3,26825	3,92190	4,57555	5,22920	5,88285
71. Terechloride of Chromium Cr Cl <sup>2</sup>	Chlorine Cl <sup>2</sup>	0,79056	1,58112	2,37168	3,16224	3,95280	4,74336	5,53392	6,32448	7,11504
72. Chloride of Arsenic As <sup>3</sup> Cl <sup>2</sup>	Chlorine Cl <sup>2</sup>	0,58551	1,17102	1,75653	2,34204	2,92755	3,51306	4,09857	4,68408	5,26959
73. Perchloride of Arsenic As <sup>3</sup> Cl <sup>2</sup>	Chlorine Cl <sup>2</sup>	0,70188	1,40376	2,10564	2,80752	3,50940	4,21128	4,91316	5,61504	6,31692
74. Chloride of Tellurium Te Cl <sup>2</sup>	Chlorine Cl <sup>2</sup>	0,35561	0,71122	1,06683	1,42244	1,77805	2,13366	2,48927	2,84488	3,20049
75. Perchloride of Tellurium Te Cl <sup>4</sup>	Chlorine Cl <sup>4</sup>	0,52465	1,04930	1,57395	2,09860	2,62325	3,14790	3,67255	4,19720	4,72185
76. Chloride of Selenium Se Cl <sup>2</sup>	Chlorine Cl <sup>2</sup>	0,30915	0,61830	0,92745	1,23660	1,54575	1,85490	2,16405	2,47320	2,78235
77. Perchloride of Selenium Se Cl <sup>4</sup>	Chlorine Cl <sup>4</sup>	0,64158	1,28316	1,92474	2,56632	3,20790	3,84948	4,49106	5,13264	5,77422
78. Chloride of Sulphur S Cl <sup>2</sup>	Chlorine Cl <sup>2</sup>	0,52386	1,04772	1,57158	2,09544	2,61930	3,14316	3,66702	4,19088	4,71474
79. Chloride of Sulphur S Cl <sup>4</sup>	Chlorine Cl <sup>4</sup>	0,81484	1,62968	2,44452	3,25936	4,07420	4,88904	5,70388	6,51872	7,33356
80. Perchloride of Sulphur S Cl <sup>6</sup>	Chlorine Cl <sup>6</sup>	0,86844	1,73688	2,60532	3,47376	4,34220	5,21064	6,07908	6,94752	7,81596

FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
<b>CHLORINE—(Continued).</b>										
81. Chloride of Phosphorus P <sup>2</sup> Cl <sub>3</sub>	Chlorine Cl <sub>2</sub>	0,77195	1,54390	2,31585	3,08780	3,85975	4,63170	5,40365	6,17560	6,94755
82. Perochloride of Phosphorus P <sup>2</sup> Cl <sub>5</sub>	Chlorine Cl <sub>2</sub>	0,84943	1,69886	2,54829	3,39772	4,24715	5,09658	5,94601	6,79544	7,64487
83. Chloride of Silicon Si Cl <sub>2</sub>	Chlorine Cl <sub>2</sub>	0,82716	1,65432	2,48148	3,30864	4,13580	4,96296	5,79012	6,61728	7,44444
84. Chloride of Tantalum Ta <sup>2</sup> Cl <sub>5</sub>	Chlorine Cl <sub>2</sub>	0,36529	0,73058	1,09587	1,46116	1,82645	2,19174	2,55703	2,92232	3,28761
85. 1° Chloride of Carbon C Cl	Chlorine Cl	0,74330	1,48660	2,22990	2,97320	3,71650	4,45980	5,20310	5,94640	6,68970
86. 2° Bichloride of Carbon C Cl <sub>2</sub>	Chlorine Cl <sub>2</sub>	0,85275	1,70550	2,55825	3,41100	4,26375	5,11650	5,96925	6,82200	7,67475
87. 3° Trichloride of Carbon C Cl <sub>3</sub>	Chlorine Cl <sub>3</sub>	0,89676	1,79352	2,69028	3,58704	4,48380	5,38056	6,27732	7,17408	8,07084
88. Chloride of Boron B Cl <sub>2</sub>	Chlorine Cl <sub>2</sub>	0,90711	1,81422	2,72133	3,62844	4,53555	5,44266	6,34977	7,25688	8,16399
89. Chloride of Bromine Br <sup>2</sup> Cl <sub>5</sub>	Chlorine Cl <sub>2</sub>	0,59188	1,38376	2,07564	2,76752	3,45940	4,15128	4,84316	5,53504	6,22692
90. Chloride of Iodine I <sup>2</sup> Cl <sub>2</sub>	Chlorine Cl <sub>2</sub>	0,58373	1,16746	1,75119	2,33492	2,91865	3,50238	4,08611	4,66984	5,25357
91. Chloride of Nitrogen N <sup>2</sup> Cl <sub>3</sub>	Chlorine Cl <sub>2</sub>	0,88237	1,76474	2,64711	3,52948	4,41185	5,29422	6,17659	7,05896	7,94133
92. Muratic Acid H <sup>2</sup> Cl <sub>2</sub>	Chlorine Cl <sub>2</sub>	0,97258	1,94516	2,91774	3,89032	4,86290	5,83548	6,80806	7,78064	8,75322
<b>XIII. CHROMIUM, Cr.</b>										
1. Oxide of Chromium Cr <sup>2</sup> O <sub>3</sub>	Chromium Cr <sup>2</sup>	0,70109	1,40217	2,10326	2,80435	3,50543	4,20652	4,90761	5,60870	6,30978



FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
COPPER—(Continued).										
4. Protoxyde of Copper Cu O . . . . .	Oxygen O . . . . .	0,20174	0,40347	0,60521	0,80695	1,00869	1,21042	1,41216	1,61390	1,81563
5. Protoxyde of Copper Cu O . . . . .	Suboxyde of Copper $\frac{1}{3}$ Cu <sub>2</sub> O . . . . .	0,89913	1,79826	2,69739	3,59652	4,49565	5,39478	6,29391	7,19304	8,09217
6. Sulphurett of Copper Cu <sub>2</sub> S . . . . .	Copper Cu <sub>2</sub> . . . . .	0,79733	1,59466	2,39199	3,18932	3,98665	4,78398	5,58131	6,37864	7,17597
7. Sulphuret of Copper Cu S . . . . .	Copper Cu . . . . .	0,66296	1,32592	1,98888	2,65184	3,31480	3,97776	4,64072	5,30368	5,96664
XVI. FLUOR, F.										
1. Fluoride of Boron B F <sub>3</sub> . . . . .	Fluorine F <sub>3</sub> . . . . .	0,39761	1,67522	2,51283	3,35044	4,18805	5,02566	5,86327	6,70088	7,53849
2. Fluoride of Silicon Si F <sub>3</sub> . . . . .	Fluorine F <sub>3</sub> . . . . .	0,71653	1,43306	2,14959	2,86612	3,58265	4,29918	5,01571	5,73224	6,44877
3. Oxygen O . . . . .	Fluorine F <sub>2</sub> . . . . .	2,33800	4,67600	7,01400	9,35200	11,69000	14,02800	16,36600	18,70400	21,04200
4. Fluoride of Boron H <sub>2</sub> F <sub>2</sub> . . . . .	Fluorine F <sub>2</sub> . . . . .	0,94933	1,89866	2,84799	3,79732	4,74665	5,69598	6,64531	7,59464	8,54397
5. Water H <sub>2</sub> O . . . . .	Hydrofluoric Acid H <sup>+</sup> F <sup>-</sup> . . . . .	2,18954	4,37908	6,56862	8,75816	10,94770	13,13724	15,32678	17,51632	19,70586
6. Fluoride of Calcium Ca F <sub>2</sub> . . . . .	Fluorine F <sub>2</sub> . . . . .	0,47732	0,95464	1,43196	1,90928	2,38660	2,86392	3,34124	3,81856	4,29588
7. Fluoride of Calcium Ca F <sub>2</sub> . . . . .	Hydrofluoric Acid H <sup>+</sup> F <sup>-</sup> . . . . .	0,50280	1,00560	1,50840	2,01120	2,51400	3,01680	3,51960	4,02240	4,52520
8. Silicfluoride of Sodium Na <sub>2</sub> F <sub>2</sub> + Si F <sub>6</sub> . . . . .	Sodium 3 Na . . . . .	0,24709	0,49418	0,74127	0,98836	1,23545	1,48254	1,72963	1,97672	2,22381
9. Fluoride of Sodium Na F . . . . .	Fluorine F <sub>2</sub> . . . . .	0,44559	0,89118	1,33677	1,78236	2,22796	2,67354	3,11913	3,56472	4,01031



FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
HYDROGEN—(Continued).										
6. Hydrofluoric Acid $H^1 F^2$ . . . . .	Hydrogen $H^2$ . . . . .	0,05067	0,10134	0,15901	0,20268	0,25335	0,30402	0,35469	0,40536	0,45603
7. Hydrocyanic Acid $H^1 + N^2 C^2$ . . . . .	Hydrogen $H^2$ . . . . .	0,03645	0,07290	0,10935	0,14580	0,18225	0,21870	0,25515	0,29160	0,32805
8. Hydrosulphuric Acid $H^1 S$ . . . . .	Hydrogen $H^2$ . . . . .	0,05842	0,11684	0,17526	0,23368	0,29210	0,35052	0,40894	0,46736	0,52578
9. Hydroseelenic Acid $H^1 Se$ . . . . .	Hydrogen $H^2$ . . . . .	0,02461	0,04922	0,07383	0,09844	0,12305	0,14766	0,17227	0,19688	0,22149
10. Hydrotelluric Acid $H^1 Te$ . . . . .	Hydrogen $H^2$ . . . . .	0,01524	0,03048	0,04572	0,06096	0,07620	0,09144	0,10668	0,12192	0,13716
11. Ammonia $H^3 N^2$ . . . . .	Hydrogen $H^2$ . . . . .	0,17456	0,34912	0,52368	0,69824	0,87280	1,04736	1,22192	1,39648	1,57104
12. Chloride of Ammonium $N^3 H^2 + H^2 Cl^2$ . . . . .	Ammonia $N^2 H^3$ . . . . .	0,32030	0,64060	0,96090	1,28120	1,60150	1,92180	2,24210	2,56240	2,88270
13. Ammonio-Chloride of Platinum $Pt Cl_4 + N^2 H^2 Cl_2 H_2$ . . . . .	Ammonia $N^2 H^3$ . . . . .	0,07692	0,15384	0,23076	0,30768	0,38460	0,46152	0,53844	0,61536	0,69228
14. Platinum $Pt$ . . . . .	Ammonia $N^2 H^3$ . . . . .	0,17390	0,34780	0,52170	0,69560	0,86950	1,04340	1,21730	1,39120	1,56510
15. Phosphuret of Hydrogen $H^2 P_2$ . . . . .	Hydrogen $H^2$ . . . . .	0,08712	0,17424	0,26136	0,34848	0,43560	0,52272	0,60984	0,69696	0,78408
16. Arsenuret of Hydrogen $H^2 As^2$ . . . . .	Hydrogen $H^2$ . . . . .	0,03830	0,07660	0,11490	0,15320	0,19150	0,22980	0,26810	0,30640	0,34470
17. 1° Carburet of Hydrogen $H_1 C$ . . . . .	Hydrogen $H^2$ . . . . .	0,24616	0,49232	0,73848	0,98464	1,23080	1,47696	1,72312	1,96928	2,21544
18. 2° Carburet of Hydrogen $H_2 C_2$ . . . . .	Hydrogen $H^2$ . . . . .	0,14036	0,28072	0,42108	0,56144	0,70180	0,84216	0,98252	1,12288	1,26324
XX. IODINE, I.										
1. Iodous Acid $I^2 O_2$ . . . . .	Iodine $I^2$ . . . . .	0,80763	1,77506	2,66260	3,55013	4,43766	5,32519	6,21272	7,10026	7,98779



FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
<b>IODINE—(Continued).</b>										
2. Iodous Acid I <sup>2</sup> O <sup>2</sup>	Oxygen O <sup>2</sup>	0,11247	0,22494	0,33740	0,44987	0,56234	0,67481	0,78728	0,89974	1,01221
3. Iodic Acid I <sup>2</sup> O <sup>3</sup>	Iodine I <sup>2</sup>	0,75942	1,51884	2,27825	3,03767	3,79709	4,55651	5,31593	6,07534	6,83476
4. Iodic Acid I <sup>2</sup> O <sup>3</sup>	Oxygen O <sup>2</sup>	0,24058	0,48116	0,72175	0,96233	1,20291	1,44349	1,68407	1,92466	2,16524
5. Oxynodic Acid I <sup>2</sup> O <sup>4</sup>	Iodine I <sup>2</sup>	0,69275	1,38550	2,07825	2,77100	3,46375	4,15650	4,84925	5,54200	6,23475
6. Oxynodic Acid I <sup>2</sup> O <sup>4</sup>	Oxygen O <sup>2</sup>	0,30725	0,61450	0,92175	1,22900	1,53625	1,84350	2,15075	2,45800	2,76525
7. Oxygen O	Iodine I <sup>2</sup>	15,78290	31,56580	47,34870	63,13160	78,91450	94,69740	110,48030	126,26320	142,04610
8. Iodide of Silver Ag I <sup>2</sup>	Iodide I <sup>2</sup>	0,53868	1,07736	1,61604	2,15472	2,69340	3,23208	3,77076	4,30944	4,84812
9. Iodide of Silver Ag I <sup>2</sup>	Hydriodic Acid H <sup>2</sup> I <sup>2</sup>	0,54294	1,08588	1,62882	2,17176	2,71470	3,25764	3,80058	4,34352	4,88646
10. Iodide of Copper Cu I	Iodine I	0,66604	1,33208	1,99812	2,66416	3,33020	3,99624	4,66228	5,32832	5,99436
11. Iodide of Copper Cu I	Hydriodic Acid H <sup>2</sup> I <sup>2</sup>	0,67130	1,34260	2,01390	2,68520	3,35650	4,02780	4,69910	5,37040	6,04170
12. Hydriodic Acid H <sup>2</sup> I <sup>2</sup>	Iodine I <sup>2</sup>	0,99216	1,98432	2,97648	3,96864	4,96080	5,95296	6,94512	7,93728	8,92944
13. Iodine I <sup>2</sup>	Oxygen O	0,06336	0,12672	0,19008	0,25344	0,31680	0,38016	0,44352	0,50688	0,57024
<b>XXI. IRIDIUM, Ia.</b>										
1. Protoxyde of Iridium Ir O	Iridium Ir	0,92500	1,84999	2,77499	3,69998	4,62498	5,54998	6,47497	7,39997	8,32496
2. Protoxyde of Iridium Ir O	Oxygen O	0,07500	0,15001	0,22501	0,30002	0,37502	0,45002	0,52503	0,60003	0,67504

FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
<b>IRIDIUM—(Continued).</b>										
3. Sesquioxide of Iridium Ir <sup>2</sup> O <sup>3</sup>	Iridium Ir <sup>2</sup>	0,89156	1,78312	2,67468	3,56624	4,45780	5,34936	6,24092	7,13248	8,02404
4. Sesquioxide of Iridium Ir <sup>2</sup> O <sup>3</sup>	Oxygen O <sup>3</sup>	0,10844	0,21688	0,32532	0,43376	0,54220	0,65064	0,75908	0,86752	0,97596
5. Binoxide of Iridium Ir O <sup>2</sup>	Iridium Ir	0,86046	1,72092	2,58137	3,44183	4,30229	5,16275	6,02321	6,88366	7,74412
6. Binoxide of Iridium Ir O <sup>2</sup>	Oxygen O <sup>2</sup>	0,13954	0,27908	0,41863	0,55817	0,69771	0,83725	0,97679	1,11634	1,25588
7. Tritoxide of Iridium Ir O <sup>3</sup>	Iridium Ir	0,80434	1,60868	2,41301	3,21735	4,02169	4,82603	5,63037	6,43470	7,23904
8. Tritoxide of Iridium Ir O <sup>3</sup>	Oxygen O <sup>3</sup>	0,19566	0,39132	0,58699	0,78265	0,97831	1,17397	1,36963	1,56530	1,76096
9. Potassio-Chlor. of Iridium Ir Cl <sup>4</sup> + K Cl <sup>2</sup>	Iridium Ir	0,40420	0,80840	1,21260	1,61680	2,02100	2,42520	2,82940	3,23360	3,63780
10. Ammonio-Chlor. of Iridium Ir Cl <sup>4</sup> + N <sup>2</sup> H <sup>2</sup> Cl <sup>2</sup> H <sup>2</sup>	Iridium Ir	0,44282	0,88464	1,32696	1,76928	2,21160	2,65392	3,09624	3,53856	3,98088
11. Iridium Ir	Chloride of Iridium Ir Cl <sup>4</sup>	1,71785	3,43570	5,15355	6,87220	8,58925	10,30710	12,02495	13,74280	15,46065
<b>XXII. IRON.</b>										
1. Protoxide of Iron Fe O	Iron Fe	0,77282	1,54464	2,31696	3,08928	3,86160	4,63392	5,40624	6,17856	6,95088
2. Protoxide of Iron Fe O	Oxygen O	0,22768	0,45536	0,68304	0,91072	1,13840	1,36608	1,59376	1,82144	2,04912
3. Peroxide of Iron Fe <sup>2</sup> O <sup>3</sup>	Iron Fe <sup>2</sup>	0,69338	1,38677	2,08015	2,77354	3,46692	4,16031	4,85369	5,54708	6,24046
4. Peroxide of Iron Fe <sup>2</sup> O <sup>3</sup>	Oxygen O <sup>2</sup>	0,30662	0,61323	0,91985	1,22646	1,53308	1,83969	2,14631	2,45292	2,75954
5. Peroxide of Iron Fe <sup>2</sup> O <sup>3</sup>	Protoxide of Iron Fe <sup>2</sup> O <sup>2</sup>	0,99780	1,99560	2,99340	3,99120	4,98900	5,98680	6,98460	7,98240	8,98020

FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
IRON—(Continued).										
6. Iron	Peroxyde of Iron	1,44220	2,89440	4,32660	5,76880	7,21100	8,65320	10,09540	11,53760	12,97980
Fe <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>									
7. Iron	Protoxyde of Iron	1,29480	2,58960	3,88440	5,17920	6,47400	7,76880	9,06360	10,35840	11,65320
Fe	Fe O									
8. Iron	Oxygen	0,29480	0,58960	0,88440	1,17920	1,47400	1,76880	2,06360	2,35840	2,65320
Fe	O									
9. Iron	Oxygen	0,44220	0,88440	1,32660	1,76880	2,21100	2,65320	3,09540	3,53760	3,97980
Fe <sup>2</sup> O	O <sup>2</sup>									
10. Oxygen	Protoxyde of Iron	8,78436	17,56852	26,35278	35,13704	43,92130	52,70556	61,48982	70,27408	79,05834
O	2 Fe O									
11. Oxygen	Protoxyde of Iron	4,39213	8,78426	13,17639	17,56852	21,96065	26,35278	30,74491	35,13704	39,52917
O	Fe O									
12. Oxygen	Peroxyde of Iron	3,26142	6,52284	9,78426	13,04568	16,30710	19,56852	22,82994	26,09136	29,35278
O <sup>2</sup>	Fe <sup>2</sup> O <sup>3</sup>									
13. Sulphur	Peroxyde of Iron	4,86380	9,72760	14,59140	19,45520	24,31900	29,18280	34,04660	38,91040	43,77420
S	Fe <sup>2</sup> O <sup>3</sup>									
14. Chlorine	Peroxyde of Iron	2,21038	4,42076	6,63114	8,84152	11,05190	13,26228	15,47266	17,68304	19,89342
Cl <sup>2</sup>	Fe <sup>2</sup> O <sup>3</sup>									
15. Gold	Protoxyde of Iron	1,06004	2,12008	3,18012	4,24016	5,30020	6,36024	7,42028	8,48032	9,54036
Au <sup>2</sup>	6 Fe O									

## OBSERVATIONS.

The 6th and 7th number of this table indicate how much peroxyde and of protoxyde of iron correspond to a found quantity of metallic iron. This kind of calculation is wanted when, in a combination of protoxyde and of peroxyde of iron, the respective quantity of the two oxides has to be determined by reducing the combination by means of sulphuretted hydrogen, the quantity of the water produced and of the iron reduced being both weighed; the experiment may be performed in two ways:—

Let us suppose, for example, that in one experiment a combination of protoxyde and of peroxyde of iron, weighing 3.449 grammes, has yielded 2.506 grammes of reduced iron and 1.061 gramme of water. Reference to the 1st series of Table XIX. will show, that the latter contains 0.943 gramme of oxygen, which quantity existed in the two oxides of iron before the experiment. The 9th series of Table XXII. shows that 2.506 grammes of metallic iron require 1.108 gramme of oxygen

OBSERVATIONS—(Continued).

to become converted into peroxide of iron. If from this quantity the operator subtracts that which existed in the water obtained (0.943), the result gives 0.165 gramme. The protoxide of iron contained in the combination would have absorbed this latter quantity of oxygen to become converted into peroxide of iron. But it is now shown by the 10th series of Table XXII., that 0.165 gramme of oxygen corresponds to 1.450 gramme of protoxide of iron; that is to say, this quantity of oxygen is necessary to convert the above quantity of protoxide of iron into peroxide of iron, whilst the 11th series indicates the oxygen contained in the protoxide of iron. If this quantity, 1.450 gramme of protoxide of iron, is deducted from 3.449 grammes, the result is 1.999 gramme of peroxide of iron.

The same result may be obtained when the quantity of the combination of proto and of peroxide of iron has not been determined by weight, but the operator merely knows that the reduction by means of hydrogen gas has given 2.506 grammes of iron and 1.061 of water. He then calculates as before the quantity of protoxide of iron at 1.450 gramme. As to that of the peroxide of iron, it is found by calculating first the oxygen contained in the protoxide of iron, either by estimating it at 0.380 from the 2nd series of Table XXII., or by doubling 0.165 gramme of oxygen, which the operator knows, by the preceding example, is necessary to convert 1.450 gramme of protoxide of iron into peroxide of iron. This quantity of oxygen is deducted from 0.943, that is to say, from the quantity of oxygen contained in the water obtained. The 0.613 gramme of oxygen which remains, and which is contained in the peroxide of iron, corresponds, according to the 12th series of Table XXII., to 1.999 gramme of peroxide of iron.

If a weighed quantity of a combination of proto and of peroxide of iron have been oxydised by means of nitric acid, and if the peroxide of iron have been precipitated by ammonia, the increase of weight which consists in oxygen may serve to calculate the quantity of protoxide of

iron from the 10th series of the table. If the quantity of the combination amounted to 3.499 grammes, and if the peroxide of iron obtained weighed 3.614 grammes, the excess 0.165 gramme of oxygen indicates, according to the 10th series, 1.450 gramme of protoxide of iron, which in the combination was united with 1.999 gramme of peroxide of iron.

When in a combination of proto and of peroxide of iron, the operator wishes to determine the quantity of the latter by means of sulphuretted hydrogen, the 13th series of Table XXII. shows to what quantity of peroxide of iron the sulphur obtained corresponds.

When in a combination of proto and of peroxide of iron the quantity of the latter has to be determined by means of silver in powder, the 14th series of the table indicates what quantity of peroxide of iron corresponds to that of the chlorine absorbed by the silver.

When in a combination of proto and of peroxide of iron the operator wishes to determine, by means of a solution of soda-chloride of gold, what quantity of protoxide of iron exists in the combination of this oxide and of peroxide of iron, the 15th series of the table gives the quantity of protoxide of iron from that of the gold obtained.

In comparing the number of the 10th, 13th, 14th, and 15th series of Table XXII., it may be seen, that whenever the quantity of protoxide and of peroxide of iron has to be determined in a combination of these two oxides by the method which consists in converting the protoxide into peroxide of iron (10th series), a very trifling error in the experiment must produce a very considerable one in the result. The error is less considerable when the peroxide of iron is determined by means of sulphuretted hydrogen; it is less still when pulverized silver is employed, and least of all when protoxide of iron is determined with soda-chloride of gold.

FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
<b>XXIII. LEAD, Pb.</b>										
1. Protoxide of Lead	Lead	0.92829	1.85658	2.78487	3.71316	4.64145	5.56974	6.49803	7.42632	8.35461
Pb O	Pb									
2. Protoxide of Lead	Oxygen	0.07171	0.14342	0.21513	0.28684	0.35855	0.43026	0.50197	0.57368	0.64539
Pb O	O									
3. Sesquioxide of Lead	Lead	0.89616	1.79232	2.68847	3.58463	4.48079	5.37695	6.27311	7.16926	8.06542
Pb <sup>2</sup> O <sup>3</sup>	Pb									
4. Sesquioxide of Lead	Oxygen	0.10384	0.20768	0.31153	0.41537	0.51921	0.62305	0.72689	0.83074	0.93458
Pb <sup>2</sup> O <sup>3</sup>	O									
5. Binoxide of Lead	Lead	0.86618	1.73235	2.59853	3.46470	4.33088	5.19706	6.06323	6.92941	7.79558
Pb O <sub>2</sub>	Pb									
6. Binoxide of Lead	Oxygen	0.13382	0.26765	0.40147	0.53530	0.66912	0.80294	0.93677	1.07059	1.20442
Pb O <sub>2</sub>	O									
7. Chloride of Lead	Lead	0.74519	1.49038	2.23545	2.98076	3.72595	4.47114	5.21633	5.96152	6.70671
Pb Cl <sub>2</sub>	Pb									
8. Chloride of Lead	Protoxide of Lead	0.80275	1.60550	2.40825	3.21100	4.01375	4.81650	5.61925	6.42200	7.22475
Pb Cl <sub>2</sub>	Pb O									
9. Sulphate of Lead	Lead	0.68287	1.36574	2.04861	2.73148	3.41435	4.09722	4.78009	5.46293	6.14583
Pb O + S O <sub>3</sub>	Pb									
10. Sulphate of Lead	Protoxide of Lead	0.73563	1.47126	2.20689	2.94252	3.67815	4.41378	5.14941	5.88504	6.62067
Pb O + S O <sub>3</sub>	Pb O									
11. Sulphuret of Lead	Lead	0.86550	1.73100	2.59650	3.46200	4.32750	5.19300	6.05850	6.92400	7.78950
Pb S	Pb									
12. Sulphuret of Lead	Protoxide of Lead	0.93236	1.86472	2.79708	3.72944	4.66180	5.59416	6.52652	7.45888	8.39124
Pb S	Pb O									
<b>XXIV. LITHIUM, L.</b>										
1. Lithia	Lithium	0.44850	0.89700	1.34550	1.79400	2.24250	2.69100	3.13950	3.58800	4.03650
L O	L									
2. Lithia	Oxygen	0.55150	1.10300	1.65450	2.20600	2.75750	3.30900	3.86050	4.41200	4.96350
L O	O									

FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
<b>LITHIUM—(Continued).</b>										
3. Sulphate of Lithia L O + S O <sub>3</sub>	Lithia L O	0.26568	0.53136	0.79704	1.06272	1.32840	1.59408	1.85976	2.12544	2.39112
4. Carbonate of Lithia L O + C O <sub>2</sub>	Lithia L O	0.39610	0.79220	1.18830	1.58440	1.98050	2.37660	2.77270	3.16880	3.56490
5. Chloride of Lithia L Cl <sub>2</sub>	Lithia L O	0.34605	0.69210	1.03815	1.38420	1.73025	2.07630	2.42235	2.76840	3.11445
6. Chloride of Lithia L Cl <sub>2</sub>	Lithium L	0.15520	0.31040	0.46560	0.62080	0.77660	0.93120	1.08640	1.24160	1.39680
7. Soda-Phosphate of Lithia (2 L O + P <sub>2</sub> O <sub>5</sub> ) + (2 Na O + P O <sub>5</sub> )	Lithia 2 L O	0.12381	0.24762	0.37143	0.49524	0.61905	0.74286	0.86667	0.99048	1.11429
<b>XXV. MAGNESIUM, Mg.</b>										
1. Magnesia Mg O	Magnesium Mg	0.61293	1.22587	1.83880	2.45173	3.06466	3.67760	4.29053	4.90346	5.51640
2. Magnesia Mg O	Oxygen O	0.38707	0.77413	1.16120	1.54827	1.93534	2.32240	2.70947	3.09654	3.48369
3. Sulphate of Magnesia Mg O + S O <sub>3</sub>	Magnesia Mg O	0.34015	0.68030	1.02045	1.36060	1.70075	2.04090	2.38105	2.72120	3.06135
4. Phosphate of Magnesia 2 Mg O + P <sub>2</sub> O <sub>5</sub>	Magnesia 2 Mg O	0.36671	0.73342	1.10013	1.46684	1.83355	2.20026	2.56697	2.93368	3.30039
5. Phosphate of Magnesia 2 Mg O + P <sub>2</sub> O <sub>5</sub>	Carbonate of Magnesia 2 Mg O + 2 C O <sub>2</sub>	0.75910	1.51820	2.27730	3.03640	3.79550	4.55460	5.31370	6.07280	6.83190
<b>XXVI. MANGANESE, Mn.</b>										
1. Protoxide of Manganese Mn O	Manganese Mn	0.77573	1.55147	2.32720	3.10294	3.87867	4.65440	5.43014	6.20587	6.98161
2. Protoxide of Manganese Mn O	Oxygen O	0.22427	0.44853	0.67280	0.89706	1.12133	1.34560	1.56986	1.79413	2.01839
3. Sesquioxide of Manganese Mn <sub>2</sub> O <sub>3</sub>	Manganese Mn <sub>2</sub>	0.69752	1.39504	2.09256	2.79008	3.48760	4.18512	4.88264	5.58016	6.27768

FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
<b>MANGANESE—(Continued).</b>										
4. Sesquioxide of Manganese Mn <sup>2</sup> O <sup>3</sup>	Oxygen O <sub>3</sub>	0,30248	0,60496	0,90744	1,20992	1,51240	1,81488	2,11736	2,41984	2,72232
5. Peroxide of Manganese Mn O <sup>2</sup>	Manganese Mn	0,63363	1,26726	1,90089	2,53452	3,16815	3,80178	4,43541	5,06904	5,70267
6. Peroxide of Manganese Mn O <sup>2</sup>	Oxygen O <sub>2</sub>	0,36637	0,73274	1,09911	1,46548	1,83185	2,19822	2,56459	2,93096	3,29733
7. Manganic Acid Mn O <sup>3</sup>	Manganese Mn	0,53553	1,07106	1,60660	2,14213	2,67766	3,21319	3,74872	4,28426	4,81979
8. Manganic Acid Mn O <sup>3</sup>	Oxygen O <sub>3</sub>	0,46447	0,92894	1,39340	1,85787	2,32234	2,78681	3,25128	3,71574	4,18021
9. Hypermanganic Acid Mn <sup>2</sup> O <sup>7</sup>	Manganese Mn <sup>2</sup>	0,49705	0,99410	1,49115	1,98820	2,48525	2,98230	3,47935	3,97640	4,47345
10. Hypermanganic Acid Mn <sup>2</sup> O <sup>7</sup>	Oxygen O <sub>7</sub>	0,50295	1,00590	1,50885	2,01180	2,51475	3,01770	3,52065	4,02360	4,52655
11. Mang.-Manganic Oxide Mn O + Mn <sup>2</sup> O <sup>3</sup>	Protox. of Manganese 3 Mn O	0,93044	1,86088	2,79132	3,72176	4,65220	5,58264	6,51308	7,44352	8,37396
12. Mang.-Manganic Oxide Mn O + Mn <sup>2</sup> O <sup>3</sup>	Sesquiox. of Manganese 1 1/2 Mn <sup>2</sup> O <sup>3</sup>	1,03478	2,06956	3,10434	4,13912	5,17390	6,20868	7,24346	8,27824	9,31302
13. Mang.-Manganic Oxide Mn O + Mn <sup>2</sup> O <sup>3</sup>	Peroxide of Manganese 3 Mn O <sup>2</sup>	1,13911	2,27822	3,41733	4,55644	5,69555	6,83466	7,97377	9,11288	10,25199
14. Sulph. of Prot. of Mang. Mn O + S O <sup>3</sup>	Protox. of Manganese Mn O	0,47082	0,94164	1,41246	1,88328	2,35410	2,82492	3,29574	3,76656	4,23738
<b>XXVII. MERCURY, Hg.</b>										
1. Suboxide of Mercury Hg <sup>2</sup> O	Mercury Hg <sup>2</sup>	0,96200	1,92400	2,88600	3,84800	4,81000	5,77201	6,73401	7,69601	8,65801
2. Suboxide of Mercury Hg <sup>2</sup> O	Oxygen O	0,03800	0,07600	0,11400	0,15200	0,19000	0,22799	0,26599	0,30399	0,34199
3. Peroxide of Mercury Hg O	Mercury Hg	0,92678	1,85357	2,78035	3,70714	4,63392	5,56070	6,48749	7,41427	8,34106

FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
<b>MOLYBDENUM—(Continued).</b>										
2. Protoxide of Molybdenum Mo O	Oxygen O	0,14316	0,28632	0,42948	0,57264	0,71580	0,85895	1,00211	1,14527	1,28843
3. Binoxide of Molybdenum Mo O <sub>2</sub>	Molybdenum Mo	0,74954	1,49908	2,24861	2,99815	3,74769	4,49723	5,24677	5,99630	6,74584
4. Binoxide of Molybdenum Mo O <sub>2</sub>	Oxygen O <sub>2</sub>	0,25046	0,50092	0,75139	1,00185	1,25231	1,50277	1,75323	2,00370	2,25416
5. Molybdic Acid Mo O <sub>3</sub>	Molybdenum Mo	0,66612	1,33224	1,99836	2,66448	3,33059	3,99671	4,66283	5,32895	5,99507
6. Molybdic Acid Mo O <sub>3</sub>	Oxygen O <sub>3</sub>	0,33388	0,66776	1,00164	1,33552	1,66941	2,00329	2,33717	2,67105	3,00493
7. 1st. Sulphuret of Molybdenum (grey) Mo S <sub>2</sub>	Molybdenum Mo	0,59802	1,19604	1,79406	2,39208	2,99010	3,58812	4,18614	4,78416	5,38218
8. 2nd. Sulph. of Molybdenum Mo S <sub>2</sub>	Molybdenum Mo	0,49793	0,99586	1,49379	1,99172	2,48965	2,98758	3,48551	3,98344	4,48137
9. Molybdenum Mo	Molybdic Acid Mo O <sub>3</sub>	1,50123	3,00246	4,50369	6,00492	7,50615	9,00738	10,50861	12,00984	13,51107
<b>XXIX. NICKEL, Ni.</b>										
1. Oxide of Nickel Ni O	Nickel Ni	0,78709	1,57417	2,36126	3,14835	3,93543	4,72252	5,50961	6,29670	7,08378
2. Oxide of Nickel Ni O	Oxygen O	0,21291	0,42583	0,63874	0,85165	1,06457	1,27748	1,49039	1,70330	1,91622
<b>XXX. NITROGEN, N.</b>										
1. Nitrous Oxide N <sub>2</sub> O	Nitrogen N <sub>2</sub>	0,63904	1,27807	1,91711	2,55614	3,19518	3,83422	4,47325	5,11229	5,75132



FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
<b>NITROGEN—(Continued).</b>										
2. Nitrous Oxide $N_2 O$	Oxygen $O$	0,36096	0,72193	1,08289	1,44386	1,80482	2,16578	2,52675	2,88771	3,24868
3. Nitric Oxide $N^2 O^2$	Nitrogen $N^2$	0,46355	0,93909	1,40864	1,87819	2,34773	2,81728	3,28683	3,75638	4,22592
4. Nitric Oxide $N^2 O^2$	Oxygen $O^2$	0,53045	1,06091	1,59136	2,12181	2,65227	3,18272	3,71317	4,24362	4,77408
5. Nitrous Acid $N^2 O^3$	Nitrogen $N^2$	0,37112	0,74223	1,11335	1,48447	1,85558	2,22670	2,59782	2,96894	3,34005
6. Nitrous Acid $N^2 O^3$	Oxygen $O^3$	0,62888	1,25777	1,88665	2,51553	3,14442	3,77330	4,40218	5,03106	5,65995
7. Nitric Acid $N^2 O^5$	Nitrogen $N^2$	0,26149	0,52297	0,78446	1,04595	1,30743	1,56892	1,83041	2,09190	2,35338
8. Nitric Acid $N^2 O^5$	Oxygen $O^5$	0,73851	1,47703	2,21554	2,95405	3,69257	4,43108	5,16959	5,90810	6,64662
9. Nitric Acid $N^2 O^5$	Nitrous Acid $N^2 O^3$	0,70459	1,40918	2,11377	2,81836	3,52295	4,22754	4,93213	5,63672	6,34131
10. Nitrate of Baryta $Ba O + N^2 O^5$	Nitric Acid $N^2 O^5$	0,41436	0,82872	1,24308	1,65744	2,07180	2,48616	2,90052	3,31488	3,72924
11. Nitrate of Baryta $Ba O + N^2 O^5$	Nitrous Acid $N^2 O^3$	0,29196	0,58392	0,87588	1,16784	1,45980	1,75176	2,04372	2,33568	2,62764
12. Sulphate of Baryta $Ba O + S O^3$	Nitric Acid $N^2 O^5$	0,46434	0,92868	1,39302	1,85736	2,32170	2,78604	3,25038	3,71472	4,17906
13. Sulphate of Baryta $Ba O + S O^3$	Nitrous Acid $N^2 O^3$	0,32718	0,65436	0,98154	1,30872	1,63590	1,96308	2,29026	2,61744	2,94462
14. Cyanogen $N^2 C^2$	Nitrogen $N^2$	0,53662	1,07324	1,60986	2,14648	2,68310	3,21972	3,75634	4,29296	4,82958
15. Cyanogen $N^2 C^2$	Carbon $C^2$	0,46338	0,92676	1,39014	1,85352	2,31690	2,78028	3,24366	3,70704	4,17042
16. Cyanide of Silver $Ag N^2 C^2$	Nitrogen $N^2$	0,19620	0,39240	0,58860	0,78480	0,98100	1,17720	1,37340	1,56960	1,76580
17. Cyanide of Mercury $Ag N^2 C^2$	Hydrocyanic Acid $N^2 C^2 H^2$	0,20362	0,40724	0,61086	0,81448	1,01810	1,22172	1,42534	1,62896	1,83258

FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
<b>XXXI. OSMIUM, Os.</b>										
1. Protoxide of Osmium Os O . . . . .	Osmium Os . . . . .	0,92561	1,85121	2,77682	3,70243	4,62803	5,55364	6,47925	7,40486	8,33046
2. Protoxide of Osmium Os O . . . . .	Oxygen O . . . . .	0,07439	0,14879	0,22318	0,29757	0,37197	0,44636	0,52075	0,59514	0,66954
3. Sesquioxide of Osmium Os <sup>3</sup> O <sup>2</sup> . . . . .	Osmium Os <sup>3</sup> . . . . .	0,89241	1,78482	2,67724	3,56965	4,46206	5,35447	6,24688	7,13930	8,03171
4. Sesquioxide of Osmium Os <sup>3</sup> O <sup>2</sup> . . . . .	Oxygen O <sup>2</sup> . . . . .	0,10759	0,21518	0,32276	0,43035	0,53794	0,64553	0,75312	0,86070	0,96829
5. Binoxide of Osmium Os O <sub>2</sub> . . . . .	Osmium Os . . . . .	0,86152	1,72303	2,58455	3,44606	4,30758	5,16910	6,03061	6,89213	7,75364
6. Binoxide of Osmium Os O <sub>2</sub> . . . . .	Oxygen O <sub>2</sub> . . . . .	0,13848	0,27697	0,41545	0,55394	0,69242	0,83090	0,96939	1,10787	1,24636
7. Osmic Acid Os O <sub>4</sub> . . . . .	Osmium Os . . . . .	0,76672	1,51344	2,27017	3,02689	3,78361	4,54033	5,29705	6,05378	6,81050
8. Osmic Acid Os O <sub>4</sub> . . . . .	Oxygen O <sub>4</sub> . . . . .	0,24328	0,48656	0,72983	0,97311	1,21639	1,45967	1,70295	1,94622	2,18950
9. Osmium Os . . . . .	Osmic Acid Os O <sub>4</sub> . . . . .	1,32149	2,64298	3,96447	5,28596	6,60745	7,92894	9,25043	10,57192	11,89341
<b>XXXII. PALLADIUM, Pd.</b>										
1. Protoxide of Palladium Pd O . . . . .	Palladium Pd . . . . .	0,86942	1,73885	2,60827	3,47770	4,34712	5,21654	6,08597	6,95539	7,82482
2. Protoxide of Palladium Pd O . . . . .	Oxygen O . . . . .	0,13058	0,26115	0,39173	0,52230	0,65288	0,78346	0,91403	1,04461	1,17518
3. Peroxide of Palladium Pd O <sub>2</sub> . . . . .	Palladium Pd . . . . .	0,76901	1,53802	2,30703	3,07604	3,84505	4,61406	5,38307	6,15208	6,92109
4. Peroxide of Palladium Pd O <sub>2</sub> . . . . .	Oxygen O <sub>2</sub> . . . . .	0,23099	0,46198	0,69297	0,92396	1,15495	1,38594	1,61693	1,84792	2,07891
5. Pot.-Chloride of Palladium K Cl <sup>2</sup> + Pd Cl <sup>2</sup> . . . . .	Palladium Pd . . . . .	0,32622	0,65244	0,97866	1,30488	1,63110	1,95732	2,28354	2,60976	2,93598

FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
<b>PALLADIUM—(Continued).</b>										
6. Palladium Pd . . . . .	Protoclor. of Palladium Pd Cl <sub>2</sub> . . . . .	1,66480	3,32960	4,99440	6,65920	8,32400	9,98880	11,65360	13,31840	14,98320
<b>XXXIII. PHOSPHORUS, P<sub>4</sub>.</b>										
1. Hypophosphorous Acid P <sub>2</sub> O . . . . .	Phosphorus P <sub>2</sub> . . . . .	0,79688	1,59376	2,39063	3,18750	3,98438	4,78126	5,57813	6,37501	7,17188
2. Hypophosphorous Acid P <sub>2</sub> O . . . . .	Oxygen O . . . . .	0,20312	0,40625	0,60937	0,81250	1,01562	1,21874	1,42187	1,62499	1,82812
3. Phosphorous Acid P <sub>2</sub> O <sub>3</sub> . . . . .	Phosphorus P <sub>2</sub> . . . . .	0,56867	1,13734	1,70600	2,26667	2,83334	3,40001	3,96668	4,53334	5,10001
4. Phosphorous Acid P <sub>2</sub> O <sub>3</sub> . . . . .	Oxygen O <sub>2</sub> . . . . .	0,43333	0,86666	1,30000	1,73333	2,16666	2,59999	3,03332	3,46666	3,89999
5. Phosphoric Acid P <sub>2</sub> O <sub>5</sub> . . . . .	Phosphorus P <sub>2</sub> . . . . .	0,43966	0,87931	1,31897	1,75863	2,19828	2,63794	3,07760	3,51726	3,95691
6. Phosphoric Acid P <sub>2</sub> O <sub>5</sub> . . . . .	Oxygen O <sub>2</sub> . . . . .	0,56034	1,12069	1,68103	2,24137	2,80172	3,36206	3,92240	4,48274	5,04309
7. Phosphoric Acid P <sub>2</sub> O <sub>5</sub> . . . . .	Hypophosphorous Acid P <sub>2</sub> O . . . . .	0,55173	1,10346	1,65519	2,20692	2,75865	3,31038	3,86211	4,41384	4,96557
8. Phosphoric Acid P <sub>2</sub> O <sub>5</sub> . . . . .	Phosphorous Acid P <sub>2</sub> O <sub>3</sub> . . . . .	0,77586	1,55172	2,32758	3,10344	3,87930	4,65516	5,43102	6,20688	6,98274
9. Phosphate of Baryta 2 Ba O + P <sub>2</sub> O <sub>5</sub> . . . . .	Phosphoric Acid P <sub>2</sub> O <sub>5</sub> . . . . .	0,31799	0,63598	0,95397	1,27196	1,58995	1,90794	2,22593	2,54392	2,86191
10. Phosphate of Lime 2 Ca O + P <sub>2</sub> O <sub>5</sub> . . . . .	Phosphoric Acid P <sub>2</sub> O <sub>5</sub> . . . . .	0,55818	1,11256	1,66854	2,22472	2,78090	3,33708	3,89326	4,44944	5,00562
11. Phosphate of Lead 2 Pb O + P <sub>2</sub> O <sub>5</sub> . . . . .	Phosphoric Acid P <sub>2</sub> O <sub>5</sub> . . . . .	0,24239	0,48478	0,72717	0,96956	1,21195	1,45434	1,69673	1,93912	2,18151
12. Phosph. of Silver (neutral) 2 Ag O + P <sub>2</sub> O <sub>5</sub> . . . . .	Phosphoric Acid P <sub>2</sub> O <sub>5</sub> . . . . .	0,23510	0,47020	0,70530	0,94040	1,17550	1,41060	1,64570	1,88080	2,11590
13. Subchloride of Mercury 8 Hg Cl . . . . .	Hypophosphorous Acid P <sub>2</sub> O . . . . .	0,04138	0,08276	0,12414	0,16552	0,20690	0,24828	0,28966	0,33104	0,37242

FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
PHOSPHORUS—(Continued).										
14. Chloride of Mercury 4 Hg Cl . . . . .	Phosphorous Acid P <sup>2</sup> O <sub>5</sub> . . . . .	0,11638	0,23276	0,34914	0,46552	0,58190	0,69828	0,81466	0,93104	1,04742
OBSERVATIONS.										
With the 13th series of this Table the operator may calculate the quantity of hypophosphorous acid from a weighed quantity of subchloride of mercury, when that substance has been precipitated from a solution of perchloride of mercury.		— With the 14th series the quantity of phosphorous acid may likewise be calculated from a quantity of subchloride of mercury obtained.								
XXXIV. PLATINUM, Pt.										
1. Protoxyde of Platinum Pt O . . . . .	Platinum Pt . . . . .	0,92500	1,84999	2,77499	3,69998	4,62498	5,54998	6,47497	7,39997	8,32496
2. Protoxyde of Platinum Pt O . . . . .	Oxygen O . . . . .	0,07500	0,15001	0,22501	0,30002	0,37502	0,45002	0,52503	0,60003	0,67504
3. Peroxyde of Platinum Pt O <sub>2</sub> . . . . .	Platinum Pt . . . . .	0,86046	1,72092	2,58137	3,44183	4,30229	5,16275	6,02321	6,88366	7,74412
4. Peroxyde of Platinum Pt O <sub>2</sub> . . . . .	Oxygen O <sub>2</sub> . . . . .	0,13954	0,27908	0,41863	0,55817	0,69771	0,83725	0,97679	1,11634	1,25588
5. Potass.-chlo. of Platinum Pt Cl <sub>3</sub> + K Cl . . . . .	Platinum Pt . . . . .	0,40420	0,80840	1,21260	1,61680	2,02100	2,42520	2,82940	3,23360	3,63780
6. Ammo.-chlo. of Platinum Pt Cl <sub>3</sub> + N <sup>3</sup> H <sup>3</sup> Cl <sub>3</sub> H <sup>2</sup> . . . . .	Platinum Pt . . . . .	0,44232	0,88464	1,32696	1,76928	2,21160	2,65392	3,09624	3,53856	3,98088
7. Platinum Pt . . . . .	Perchlor. of Platinum Pt Cl <sub>4</sub> . . . . .	1,71785	3,43570	5,15355	6,87140	8,58925	10,30710	12,02495	13,74280	15,46065
XXXV. POTASSIUM, K.										
1. Potash K O . . . . .	Potassium K . . . . .	0,83048	1,66097	2,49145	3,32194	4,15242	4,98290	5,81339	6,64387	7,47436



FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
<b>XXXVII. SELENIUM, Sz.</b>										
1. Selenious Acid Se O <sub>3</sub> . . . . .	Selenium Se . . . . .	0,71206	1,42411	2,13617	2,84823	3,56028	4,27234	4,98440	5,69646	6,40851
2. Selenious Acid Se O <sub>3</sub> . . . . .	Oxygen O <sub>3</sub> . . . . .	0,28794	0,57589	0,86383	1,15177	1,43972	1,72766	2,01560	2,30354	2,59149
3. Selenic Acid Se O <sub>4</sub> . . . . .	Selenium Se . . . . .	0,62244	1,24489	1,86733	2,48977	3,11221	3,73466	4,35710	4,97954	5,60199
4. Selenic Acid Se O <sub>4</sub> . . . . .	Oxygen O <sub>4</sub> . . . . .	0,37756	0,75511	1,13267	1,51023	1,88779	2,26534	2,64290	3,02046	3,39801
5. Sulphuret of Selenium Se S <sub>2</sub> . . . . .	Selenium Se . . . . .	0,55143	1,10286	1,65429	2,20572	2,75715	3,30858	3,86001	4,41144	4,96287
6. Sulphuret of Selenium Se S <sub>2</sub> . . . . .	Selenious Acid Se O <sub>3</sub> . . . . .	0,77442	1,54884	2,32326	3,09768	3,87210	4,64652	5,42094	6,19536	6,96978
7. Selenium Se . . . . .	Selenious Acid Se O <sub>3</sub> . . . . .	1,40438	2,80876	4,21314	5,61752	7,02190	8,42628	9,83066	11,23504	12,63942
8. Selenium Se . . . . .	Selenic Acid Se O <sub>4</sub> . . . . .	1,60657	3,21314	4,81971	6,42628	8,03285	9,63942	11,24599	12,85256	14,45913
9. Seleniate of Baryta Ba O + Se O <sub>3</sub> . . . . .	Selenic Acid Se O <sub>4</sub> . . . . .	0,45367	0,90734	1,36101	1,81468	2,26835	2,72202	3,17569	3,62936	4,08303
10. Seleniate of Baryta Ba O + Se O <sub>3</sub> . . . . .	Selenious Acid Se O <sub>3</sub> . . . . .	0,39657	0,79314	1,18971	1,58628	1,98285	2,37942	2,77599	3,17256	3,56913
<b>XXXVIII. SILICIUM, Si.</b>										
1. Silicic Acid Si O <sub>2</sub> . . . . .	Silicium Si . . . . .	0,48050	0,96100	1,44150	1,92200	2,40250	2,88300	3,36350	3,84400	4,32500
2. Silicic Acid Si O <sub>2</sub> . . . . .	Oxygen O <sub>2</sub> . . . . .	0,51950	1,03900	1,55850	2,07800	2,59750	3,11700	3,63650	4,15600	4,67500
<b>XXXIX. SILVER, Ag.</b>										
1. Oxide of Silver Ag O . . . . .	Silver Ag . . . . .	0,93111	1,86222	2,79333	3,72444	4,65555	5,58667	6,51778	7,44889	8,38000



FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
<b>STRONTIUM—(Continued).</b>										
2. Strontia Sr O	Oxygen O	0,15449	0,30898	0,46347	0,61796	0,77245	0,92694	1,08143	1,23592	1,39041
3. Sulphate of Strontia Sr O + S O <sub>2</sub>	Strontia Sr O	0,56360	1,12720	1,69080	2,25440	2,81800	3,38160	3,94520	4,50880	5,07240
4. Carbonate of Strontia Sr O + C O <sub>2</sub>	Strontia Sr O	0,70074	1,40148	2,10222	2,80296	3,50370	4,20444	4,90518	5,60592	6,30666
5. Nitrate of Strontia Sr O + N <sub>2</sub> O <sub>5</sub>	Strontia Sr O	0,48877	0,97754	1,46631	1,95508	2,44385	2,93262	3,42139	3,91016	4,39893
6. Chloride of Strontium Sr Cl <sub>2</sub>	Strontia Sr O	0,65387	1,30774	1,96161	2,61548	3,26935	3,92322	4,57709	5,23096	5,88483
7. Chloride of Strontium Sr Cl <sub>2</sub>	Strontium Sr	0,55285	1,10570	1,65855	2,21140	2,76425	3,31710	3,86995	4,42280	4,97565
<b>XLIII. SULPHUR, S.</b>										
1. Hyposulphurous Acid Sr O <sub>2</sub>	Sulphur S	0,66796	1,33591	2,00387	2,67182	3,33978	4,00774	4,67569	5,34365	6,01160
2. Hyposulphurous Acid Sr O <sub>2</sub>	Oxygen O <sub>2</sub>	0,33204	0,66409	0,99613	1,32818	1,66022	1,99226	2,32431	2,65635	2,98840
3. Sulphurous Acid Sr O <sub>2</sub>	Sulphur S	0,50145	1,00290	1,50436	2,00581	2,50726	3,00871	3,51016	4,01162	4,51307
4. Sulphurous Acid Sr O <sub>2</sub>	Oxygen O <sub>2</sub>	0,49855	0,99710	1,49564	1,99419	2,49274	2,99129	3,48984	3,98838	4,48693
5. Hyposulphuric Acid Sr O <sub>3</sub>	Sulphur S	0,44868	0,89176	1,33764	1,78352	2,22939	2,67527	3,12115	3,56703	4,01291
6. Hyposulphuric Acid Sr O <sub>3</sub>	Oxygen O <sub>3</sub>	0,55412	1,10824	1,66236	2,21648	2,77061	3,32473	3,87885	4,43297	4,98709
7. Sulphuric Acid Sr O <sub>3</sub>	Sulphur S	0,40139	0,80279	1,20418	1,60558	2,00697	2,40837	2,80976	3,21116	3,61255
8. Sulphuric Acid Sr O <sub>3</sub>	Oxygen O <sub>3</sub>	0,59861	1,19721	1,79582	2,39442	2,99303	3,59163	4,19024	4,78884	5,38745



FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
SULPHUR—(Continued).										
9. Sulphate of Baryta Ba O + SO <sub>3</sub> .	Sulphur S	0,13797	0,27594	0,41391	0,55188	0,68985	0,82782	0,96579	1,10376	1,24173
10. Sulphate of Baryta 2 (Ba O + S O <sub>3</sub> ).	Hypo-sulphurous Acid S <sup>2</sup> O <sub>3</sub>	0,20655	0,41310	0,61965	0,82620	1,03275	1,23930	1,44585	1,65240	1,85895
11. Sulphate of Baryta Ba O + S O <sub>3</sub> .	Hypo-sulphurous Acid S <sup>2</sup> O <sub>3</sub> .	0,41310	0,82620	1,23930	1,65240	2,06550	2,47860	2,89170	3,30480	3,71790
12. Sulphate of Baryta Ba O + S O <sub>3</sub> .	Sulphurous Acid S O <sub>3</sub> .	0,27514	0,55028	0,82542	1,10056	1,37570	1,65084	1,92598	2,20112	2,47626
13. Sulphate of Baryta Ba O + S O <sub>3</sub> .	Hypo-sulphuric Acid S <sup>2</sup> O <sub>4</sub> .	0,30943	0,61886	0,92829	1,23772	1,54715	1,85658	2,16601	2,47544	2,78487
14. Sulphate of Baryta Ba O + S O <sub>3</sub> .	Sulphuric Acid S O <sub>3</sub> .	0,34372	0,68744	1,03116	1,37488	1,71860	2,06232	2,40604	2,74976	3,09348
15. Sulphate of Lime Ca O + S O <sub>3</sub> .	Sulphuric Acid S O <sub>3</sub> .	0,58468	1,16936	1,75404	2,33872	2,92340	3,50808	4,09276	4,67744	5,26212
16. Sulphate of Lead Pb O + S O <sub>3</sub> .	Sulphur S	0,10612	0,21224	0,31836	0,42448	0,53060	0,63672	0,74284	0,84896	0,95508
17. Sulphate of Lead Pb O + S O <sub>3</sub> .	Sulphuric Acid S O <sub>3</sub> .	0,26437	0,52874	0,79311	1,05748	1,32185	1,58622	1,85059	2,11496	2,37933
18. Sulphuret of Silver Ag S	Hypo-sulphuric Acid S <sup>2</sup> O <sub>3</sub> .	0,38791	0,77582	1,16373	1,55164	1,93955	2,32746	2,71537	3,10328	3,49119
19. 1st. Sulphuret of Potassium K S	Sulphur S	0,29109	0,58218	0,87327	1,16436	1,45545	1,74654	2,03763	2,32872	2,61981
20. 2nd. Sulphuret of Potassium K S <sub>2</sub> .	Sulphur S	0,45092	0,90184	1,35276	1,80368	2,25460	2,70552	3,15644	3,60736	4,05828
21. 3rd. Sulphuret of Potassium K S <sub>3</sub> .	Sulphur S	0,55194	1,10388	1,65582	2,20776	2,75970	3,31164	3,86358	4,41552	4,96746
22. 4th. Sulphuret of Potassium K <sup>3</sup> S <sub>4</sub> .	Sulphur S	0,58968	1,17936	1,76904	2,35872	2,94840	3,53808	4,12776	4,71744	5,30712
23. 5th. Sulphuret of Potassium K S <sub>4</sub> .	Sulphur S	0,62156	1,24312	1,86468	2,48624	3,10780	3,72936	4,35092	4,97248	5,59404
24. 6th. Sulphuret of Potassium K <sub>2</sub> S <sub>6</sub> .	Sulphur S <sub>6</sub> .	0,64885	1,29770	1,94655	2,59540	3,24425	3,89310	4,54195	5,19080	5,83965

FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
SULPHUR—(Continued).										
25. 7th. Sulphuret of Potassium K S <sub>5</sub> .	Sulphur S <sub>5</sub> .	0,67246	1,34492	2,01738	2,68984	3,36230	4,03476	4,70722	5,37968	6,05214
26. 1st. Sulphuret of Sodium Na S.	Sulphur S.	0,40882	0,81764	1,22646	1,63528	2,04410	2,45292	2,86174	3,27056	3,67938
27. 2nd. Sulphuret of Sodium Na S <sub>2</sub> .	Sulphur S <sub>2</sub> .	0,58037	1,16074	1,74111	2,32148	2,90185	3,48222	4,06259	4,64296	5,22333
28. Sulphuret of Lithium Li S.	Sulphur S.	0,71213	1,42426	2,13639	2,84852	3,56065	4,27278	4,98491	5,69704	6,40917
29. Sulphuret of Barium Ba S.	Sulphur S.	0,19013	0,38026	0,57039	0,76052	0,95065	1,14078	1,33091	1,52104	1,71117
30. Sulphuret of Strontium Sr S.	Sulphur S.	0,26878	0,53756	0,80634	1,07512	1,34390	1,61268	1,88146	2,15024	2,41902
31. Sulphur of Calcium Ca S.	Sulphur S.	0,44001	0,88002	1,32003	1,76004	2,20005	2,64006	3,08007	3,52008	3,96009
32. Sulphur of Magnesium Mg S.	Sulphur S.	0,55954	1,11908	1,67862	2,23816	2,79770	3,35724	3,91678	4,47632	5,03586
33. Sulphuret of Aluminium Al <sub>2</sub> S <sub>3</sub> .	Sulphur S <sub>3</sub> .	0,63806	1,27612	1,91418	2,55224	3,19030	3,82836	4,46642	5,10448	5,74254
34. Sulphuret of Glucinium Be <sup>2</sup> S <sub>3</sub> .	Sulphur S <sub>3</sub> .	0,47652	0,95304	1,42956	1,90608	2,38260	2,85912	3,33564	3,81216	4,28868
35. Sulphuret of Thorium Th S.	Sulphur S.	0,21263	0,42526	0,63789	0,85052	1,06315	1,27578	1,48841	1,70104	1,91367
36. Sulphuret of Yttrium Y S.	Sulphur S.	0,33360	0,66720	1,00080	1,33440	1,66800	2,00160	2,33520	2,66880	3,00240
37. 1st. Sulphuret of Cerium Ce S.	Sulphur S.	0,41178	0,82356	1,23534	1,64712	2,05890	2,47068	2,88246	3,29424	3,70602
38. 2nd. Sulphuret of Cerium Ce <sup>2</sup> S <sub>2</sub> .	Sulphur S <sub>2</sub> .	0,51221	1,02442	1,53663	2,04884	2,56105	3,07326	3,58547	4,09768	4,60989
39. Sulphuret of Zirconium Zr <sup>2</sup> S <sub>2</sub> .	Sulphur S <sub>2</sub> .	0,41794	0,83588	1,25382	1,67176	2,08970	2,50764	2,92558	3,34352	3,76146
40. Sulphuret of Manganese Mn S.	Sulphur S.	0,36772	0,73544	1,10316	1,47088	1,83860	2,20632	2,57404	2,94176	3,30948

FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
SULPHUR—(Continued).										
41. 1st. Sulphuret of Iron Fe S	Sulphur S	0.37227	0.74454	1.11681	1.48908	1.86135	2.23362	2.60589	2.97816	3.35045
42. 2nd. Sulphuret of Iron Fe <sup>2</sup> S <sub>3</sub>	Sulphur S <sub>3</sub>	0.47077	0.94154	1.41231	1.88308	2.35385	2.82462	3.29539	3.76616	4.23693
43. 3rd. Sulph. of Iron (Pyrites) Fe <sup>3</sup> S <sub>4</sub>	Sulphur S <sub>4</sub>	0.54256	1.08512	1.62768	2.17024	2.71280	3.25536	3.79792	4.34048	4.88304
44. Sulphuret of Zinc Zn S	Sulphur S	0.33284	0.66568	0.99852	1.33136	1.66420	1.99704	2.32988	2.66272	2.99556
45. 1st. Sulphuret of Cobalt Co S	Sulphur S	0.35292	0.70584	1.05846	1.41128	1.76410	2.11692	2.46974	2.82256	3.17538
46. 2nd. Sulphuret of Cobalt Co <sup>2</sup> S <sub>3</sub>	Sulphur S <sub>3</sub>	0.44987	0.89974	1.34961	1.79948	2.24935	2.69922	3.14909	3.59896	4.04883
47. 3rd. Sulphuret of Cobalt Co <sup>3</sup> S <sub>4</sub>	Sulphur S <sub>4</sub>	0.52161	1.04322	1.56483	2.08644	2.60805	3.12966	3.65127	4.17288	4.69449
48. 1st. Sulphuret of Nickel Ni <sup>2</sup> S	Sulphur S	0.21389	0.42778	0.64167	0.85556	1.06945	1.28334	1.49723	1.71112	1.92501
49. 2nd. Sulphuret of Nickel Ni S	Sulphur S	0.35240	0.70480	1.05720	1.40960	1.76200	2.11440	2.46680	2.81920	3.17160
50. Sulphuret of Cadmium Cd S	Sulphur S	0.22403	0.44806	0.67209	0.89612	1.12015	1.34418	1.56821	1.79224	2.01627
51. 1st. Sulphuret of Lead Pb <sup>2</sup> S	Sulphur S	0.03740	0.07480	0.11220	0.14960	0.18700	0.22440	0.26180	0.29920	0.33660
52. 2nd. Sulphuret of Lead Pb S	Sulphur S	0.07210	0.14420	0.21630	0.28840	0.36050	0.43260	0.50470	0.57680	0.64890
53. 3rd. Sulphuret of Lead Pb <sup>3</sup> S <sub>3</sub>	Sulphur S <sub>3</sub>	0.13450	0.26900	0.40350	0.53800	0.67250	0.80700	0.94150	1.07600	1.21050
54. Sulphuret of Bismuth Bi S	Sulphur S	0.18488	0.36976	0.55464	0.73952	0.92440	1.10928	1.29416	1.47904	1.66392
55. Sulphuret of Uranium U S	Sulphur S	0.06907	0.13814	0.20721	0.27628	0.34535	0.41442	0.48349	0.55256	0.62163
56. 1st. Sulphuret of Copper Cu <sup>2</sup> S	Sulphur S	0.20267	0.40534	0.60801	0.81068	1.01335	1.21602	1.41869	1.62186	1.82403

FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
SULPHUR—(Continued).										
57. 2nd. Sulphuret of Copper	Sulphur S	0,33704	0,67408	1,01112	1,34816	1,68520	2,02224	2,35928	2,69632	3,03336
58. Sulphuret of Silver	Sulphur S	0,12055	0,25910	0,38865	0,51820	0,64775	0,77730	0,90685	1,03640	1,16595
59. 1st. Sulphuret of Mercury	Sulphur S	0,07361	0,14722	0,22083	0,29444	0,36805	0,44166	0,51527	0,58888	0,66249
60. 2nd. Sulphuret of Mercury	Sulphur S	0,13713	0,27426	0,41139	0,54852	0,68565	0,82278	0,95991	1,09704	1,23417
61. Sulphuret of Rhodium	Sulphur S	0,23395	0,47190	0,70785	0,94380	1,17975	1,41570	1,65165	1,88760	2,12355
62. Sulphuret of Palladium	Sulphur S	0,23202	0,46404	0,69606	0,92808	1,16010	1,39212	1,62414	1,85616	2,08818
63. Sulphuret of Iridium	Sulphur S	0,14024	0,28048	0,42072	0,56096	0,70120	0,84144	0,98168	1,12192	1,26216
64. Sulphuret of Osmium	Sulphur S	0,24435	0,48870	0,73305	0,97740	1,22175	1,46610	1,71045	1,95480	2,19915
65. 1st. Sulphuret of Platinum	Sulphur S	0,14024	0,28048	0,42072	0,56096	0,70120	0,84144	0,98168	1,12192	1,26216
66. 2nd. Sulphuret of Platinum	Sulphur S	0,24398	0,49196	0,73794	0,98392	1,22990	1,47588	1,72186	1,96784	2,21382
67. Sulphuret of Gold	Sulphur S	0,19534	0,39068	0,58602	0,78136	0,97670	1,17204	1,36738	1,56272	1,75806
68. 1st. Sulphuret of Tin	Sulphur S	0,21481	0,42962	0,64443	0,85924	1,07405	1,28886	1,50367	1,71848	1,93329
69. 2nd. Sulphuret of Tin	Sulphur S	0,29097	0,58194	0,87291	1,16388	1,45485	1,74582	2,03679	2,32776	2,61873
70. 3rd. Sulphuret of Tin	Sulphur S	0,35366	0,70732	1,06098	1,41464	1,76830	2,12196	2,47562	2,82928	3,18294
71. Sulphuret of Titanium	Sulphur S	0,56986	1,13972	1,70958	2,27944	2,84930	3,41916	3,98902	4,55888	5,12874
72. 1st. Sulphuret of Antimony	Sulphur S	0,27229	0,54458	0,81687	1,08916	1,36145	1,63374	1,90603	2,17832	2,45061

FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
SULPHUR—(Continued).										
73. 2nd. Sulphuret of Antimony Sb <sup>2</sup> S <sub>3</sub>	Sulphur S <sub>4</sub>	0,33284	0,66568	0,99852	1,33136	1,66420	1,99704	2,32988	2,66272	2,99556
74. 3rd. Sulphuret of Antimony Sb <sup>2</sup> S <sub>5</sub>	Sulphur S <sub>5</sub>	0,38409	0,76818	1,15227	1,53636	1,92045	2,30454	2,68863	3,07272	3,45681
75. 1st. Sulphuret of Tungsten W S <sub>2</sub>	Sulphur S <sub>3</sub>	0,25375	0,50750	0,76125	1,01500	1,26875	1,52250	1,77625	2,03000	2,28375
76. 2nd. Sulphuret of Tungsten W S <sub>3</sub>	Sulphur S <sub>3</sub>	0,33777	0,67554	1,01331	1,35108	1,68885	2,02662	2,36439	2,70216	3,03993
77. 1st. Sulph. of Molybdenum Mo S <sub>2</sub>	Sulphur S <sub>3</sub>	0,40199	0,80398	1,20597	1,60796	2,00995	2,41194	2,81393	3,21592	3,61791
78. 2nd. Sulph. of Molybdenum Mo S <sub>3</sub>	Sulphur S <sub>3</sub>	0,50207	1,00414	1,50621	2,00828	2,51035	3,01242	3,51449	4,01656	4,51863
79. 3rd. Sulph. of Molybdenum Mo S <sub>4</sub>	Sulphur S <sub>4</sub>	0,57345	1,14690	1,72035	2,29380	2,86725	3,44070	4,01415	4,58760	5,16105
80. 1st. Sulphuret of Vanadium V S <sub>2</sub>	Sulphur S <sub>3</sub>	0,31977	0,63954	0,95931	1,27908	1,59885	1,91862	2,23839	2,55816	2,87793
81. 2nd. Sulphuret of Vanadium V S <sub>3</sub>	Sulphur S <sub>3</sub>	0,41354	0,82708	1,24062	1,65416	2,06770	2,48124	2,89478	3,30832	3,72186
82. Sulphuret of Chromium Cr <sup>2</sup> S <sub>3</sub>	Sulphur S <sub>3</sub>	0,46169	0,92338	1,38507	1,84676	2,30845	2,77014	3,23183	3,69352	4,15521
83. 1st. Sulphuret of Arsenic As <sup>2</sup> S <sub>3</sub>	Sulphur S <sub>3</sub>	0,03444	0,06888	0,10332	0,13776	0,17220	0,20664	0,24108	0,27552	0,30996
84. 2nd. Sulphuret of Arsenic As <sup>2</sup> S <sub>4</sub>	Sulphur S <sub>4</sub>	0,29971	0,59942	0,89913	1,19884	1,49855	1,79826	2,09797	2,39768	2,69739
85. 3rd. Sulphuret of Arsenic As <sup>2</sup> S <sub>5</sub>	Sulphur S <sub>5</sub>	0,39097	0,78194	1,17291	1,56388	1,95485	2,34582	2,73679	3,12776	3,51873
86. 4th. Sulphuret of Arsenic As <sup>2</sup> S <sub>6</sub>	Sulphur S <sub>6</sub>	0,51689	1,03378	1,55067	2,06756	2,58445	3,10134	3,61823	4,13512	4,65201
87. 5th. Sulphuret of Arsenic As <sup>2</sup> S <sub>7</sub>	Sulphur S <sub>7</sub>	0,79339	1,58678	2,38167	3,17556	3,96945	4,76334	5,55723	6,35112	7,14501
88. Sulphuret of Tellurium Te S <sub>2</sub>	Sulphur S <sub>2</sub>	0,33404	0,66808	1,00212	1,33616	1,67020	2,00424	2,33828	2,67232	3,00636

FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
SULPHUR—(Continued).										
89. Sulphuret of Selenium Se S <sub>8</sub> . . . . .	Sulphur S <sub>8</sub> . . . . .	0,44857	0,89714	1,34571	1,79428	2,24285	2,69142	3,13999	3,58856	4,03713
90. Sulphuret of Silicon Si S <sub>8</sub> . . . . .	Sulphur S <sub>8</sub> . . . . .	0,68503	1,37006	2,05509	2,74012	3,42515	4,11018	4,79521	5,48024	6,16527
91. Sulphuret of Tantalum Ta S <sub>8</sub> . . . . .	Sulphur S <sub>8</sub> . . . . .	0,25856	0,51712	0,77568	1,03424	1,29280	1,55136	1,80992	2,06848	2,32704
92. Sulphuret of Carbon C S <sub>8</sub> . . . . .	Sulphur S <sub>8</sub> . . . . .	0,84035	1,68070	2,52105	3,36140	4,20175	5,04210	5,88245	6,72280	7,56315
93. Sulphuret of Boron B S <sub>8</sub> (?) . . . . .	Sulphur S <sub>8</sub> . . . . .	0,74739	1,49478	2,24217	2,98956	3,73695	4,48434	5,23173	5,97912	6,72651
94. Sulphuret of Water H <sup>2</sup> S . . . . .	Sulphur S . . . . .	0,94159	1,88318	2,82477	3,76636	4,70795	5,64954	6,59113	7,53272	8,47431

## OBSERVATIONS.

The 10th series of this Table indicates how the operator may, from a known quantity of sulphate of baryta, calculate that of the hyposulphurous acid contained in a hyposulphite when the hyposulphurous acid of this salt has been entirely converted into sulphuric acid by nitrate or chlorate of potash.

The 11th series shows how the hyposulphurous acid of a hyposulphite can be calculated from a known quantity of sulphate of baryta when the solution of the salt has been decomposed by a solution of silver, half of the sulphur of the acid having been thereby converted into sulphuric

acid, which has been precipitated as sulphate of baryta by means of a barytic salt.

The 18th series shows how to calculate the quantity of hyposulphurous acid in a hyposulphite from a known quantity of sulphuret of silver, when the solution of the salt has been decomposed by a solution of silver.

The 51st and 52nd series indicate the quantities of sulphur contained in the newly-discovered combinations of sulphur and of lead.

## XLIII. TANTALUM, Ta.

1. Oxide of Tantalum Ta O . . . . .	Tantalum Ta . . . . .	1,84047	2,76071	3,68095	4,60118	5,52142	6,44166	7,36190	8,28218
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FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
<b>TANTALUM—(Continued).</b>										
2. Oxide of Tantalum Ta <sub>2</sub> O <sub>5</sub> . . . . .	Oxygen O . . . . .	0,07976	0,15953	0,23929	0,31905	0,39882	0,47858	0,55834	0,63810	0,71787
3. Tantalic Acid Ta <sub>2</sub> O <sub>5</sub> . . . . .	Tantalum Ta <sub>2</sub> . . . . .	0,88494	1,76989	2,65483	3,53978	4,42472	5,30966	6,19461	7,07955	7,96450
4. Tantalic Acid Ta <sub>2</sub> O <sub>5</sub> . . . . .	Oxygen O <sub>3</sub> . . . . .	0,11506	0,23011	0,34517	0,46022	0,57528	0,69034	0,80539	0,92045	1,03550
<b>XLIV. TELLURIUM, Te.</b>										
1. Tellurous Acid Te O <sub>2</sub> . . . . .	Tellurium Te . . . . .	0,80042	1,60084	2,40126	3,20168	4,00210	4,80252	5,60294	6,40336	7,20378
2. Tellurous Acid Te O <sub>2</sub> . . . . .	Oxygen O <sub>2</sub> . . . . .	0,19958	0,39916	0,59874	0,79832	0,99790	1,19748	1,39706	1,59664	1,79622
3. Telluric Acid Te O <sub>3</sub> . . . . .	Tellurium Te . . . . .	0,72780	1,45560	2,18340	2,91120	3,63900	4,36680	5,09460	5,82240	6,55020
4. Telluric Acid Te O <sub>3</sub> . . . . .	Oxygen O <sub>3</sub> . . . . .	0,27220	0,54440	0,81660	1,08880	1,36100	1,63320	1,90540	2,17760	2,44980
5. Tellurium Te . . . . .	Tellurous Acid Te O <sub>2</sub> . . . . .	1,24934	2,49868	3,74802	4,99736	6,24670	7,49604	8,74538	9,99472	11,24406
6. Sulphuret of Tellurium Te S <sub>2</sub> . . . . .	Tellurium Te . . . . .	0,66596	1,33192	1,99788	2,66384	3,32980	3,99576	4,66172	5,32768	5,99364
7. Sulphuret of Tellurium Te S <sub>2</sub> . . . . .	Tellurous Acid Te O <sub>2</sub> . . . . .	0,83201	1,66402	2,49603	3,32804	4,16005	4,99206	5,82407	6,65608	7,48809
<b>XLV. THORINIUM, Th.</b>										
1. Thorina Th O . . . . .	Thorium Th . . . . .	0,88164	1,76329	2,64493	3,52657	4,40821	5,28986	6,17150	7,05314	7,93479
2. Thorina Th O . . . . .	Oxygen O . . . . .	0,11836	0,23671	0,35507	0,47343	0,59179	0,71014	0,82850	0,94686	1,06521

FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
<b>XLVI. TIN, Sn.</b>										
1. Protoxide of Tin	Tin	0.88028	1.76056	2.64085	3.52113	4.40141	5.28169	6.16197	7.04226	7.92254
Sn O . . . . .	Sn									
2. Protoxide of Tin	Oxygen	0.11972	0.23944	0.35915	0.47887	0.59859	0.71831	0.83803	0.95774	1.07746
Sn O . . . . .	O									
3. Peroxide of Tin	Tin	0.78616	1.57233	2.35849	3.14466	3.93082	4.71698	5.50315	6.28931	7.07547
Sn O <sub>2</sub> . . . . .	Sn									
4. Peroxide of Tin	Oxygen	0.21384	0.42767	0.64151	0.85534	1.06916	1.28302	1.49685	1.71069	1.92458
Sn O <sub>2</sub> . . . . .	O									
5. Peroxide of Tin	Protoxide of Tin	0.89308	1.78616	2.67924	3.57232	4.46540	5.35848	6.25156	7.14464	8.03772
Sn O <sub>2</sub> . . . . .	Sn O									
6. Sulphuret of Tin	Tin	0.64634	1.29268	1.93902	2.58536	3.23170	3.87804	4.52438	5.17072	5.81706
Sn S <sub>2</sub> . . . . .	Sn									
7. Sulphuret of Tin	Protoxide of Tin	0.73425	1.46850	2.20275	2.93700	3.67125	4.40550	5.13975	5.87400	6.60825
Sn S <sub>2</sub> . . . . .	Sn O									
8. Sulphuret of Tin	Peroxide of Tin	0.82215	1.64430	2.46645	3.28860	4.11075	4.93290	5.75505	6.57720	7.39935
Sn S <sub>2</sub> . . . . .	Sn O <sub>2</sub>									
9. Subchloride of Mercury	Protoxide of Tin	0.28084	0.56168	0.84252	1.12336	1.40420	1.68504	1.96588	2.24672	2.52756
2 Hg Cl . . . . .	Sn O									
10. Subchloride of Mercury	Chloride of Tin	0.39604	0.79208	1.18812	1.58416	1.98020	2.37624	2.77228	3.16832	3.56436
2 Hg C . . . . .	Sn Cl <sub>2</sub>									
<b>XLVII. TITANIUM, Ti.</b>										
1. Titanic Acid	Titanium	0.60293	1.20585	1.80878	2.41171	3.01463	3.61756	4.22049	4.82342	5.42634
Ti O <sub>2</sub> . . . . .	Ti									

## OBSERVATIONS.

The numbers 9 and 10 of this Table refer to what has been said in the quantity of subchloride of mercury obtained, that of the protoxide respecting the determination of protoxide and protochloride of tin when they exist mixed with peroxide and perchloride of tin. From the quantity of subchloride of mercury obtained, that of the protoxide of tin and of the protochloride of tin may be calculated.





FOUND.	REQUIRED.	1.	2.	3.	4.	5.	6.	7.	8.	9.
<b>VANADIUM—(Continued).</b>										
2. Oxide of Vanadium V O	Oxygen O	0,10462	0,20924	0,31386	0,41848	0,52310	0,62772	0,73234	0,83696	0,94158
3. Binoxide of Vanadium V O <sub>2</sub>	Vanadium V	0,81058	1,62116	2,43174	3,24232	4,05290	4,86348	5,67406	6,48464	7,29522
4. Binoxide of Vanadium V O <sub>2</sub>	Oxygen O <sub>2</sub>	0,18942	0,37884	0,56826	0,75768	0,94710	1,13652	1,32594	1,51536	1,70478
5. Vanadic Acid V O <sub>3</sub>	Vanadium V	0,74045	1,48090	2,22135	2,96180	3,70225	4,44270	5,18315	5,92360	6,66405
6. Vanadic Acid V O <sub>3</sub>	Oxygen O <sub>3</sub>	0,25955	0,51910	0,77865	1,03820	1,29775	1,55730	1,81685	2,07640	2,33595
<b>LI. YTTRIUM, Y.</b>										
1. Ytria Y O	Yttrium Y	0,80073	1,60147	2,40220	3,20293	4,00366	4,80440	5,60513	6,40586	7,20660
2. Ytria Y O	Oxygen O	0,19927	0,39853	0,59780	0,79707	0,99634	1,19560	1,39487	1,59414	1,79340
<b>LII. ZINC, Zn.</b>										
1. Oxide of Zinc Zn O	Zinc Zn	0,80128	1,60256	2,40385	3,20513	4,00641	4,80769	5,60897	6,41026	7,21154
2. Oxide of Zinc Zn O	Oxygen O	0,19872	0,39744	0,59615	0,79487	0,99359	1,19231	1,39103	1,58974	1,78846
3. Sulphate of Zinc Zn O + S O <sub>2</sub>	Oxide of Zinc Zn O	0,50103	1,00206	1,50309	2,00412	2,50515	3,00618	3,50721	4,00824	4,50927
<b>LIII. ZIRCONIUM, Zr.</b>										
1. Zirconia Zr <sup>2</sup> O <sub>2</sub>	Zirconium Zr <sup>2</sup>	0,73695	1,47390	2,21086	2,94781	3,68476	4,42171	5,15865	5,89560	6,63255
2. Zirconia Zr <sup>2</sup> O <sub>2</sub>	Oxygen O <sub>2</sub>	0,26305	0,52610	0,78914	1,05219	1,31524	1,57829	1,84135	2,10440	2,36745



## TABLE

OF THE SPECIFIC AND ABSOLUTE GRAVITY OF THE MOST IMPORTANT GASES, AND OF THE RESPECTIVE COMPOSITION AND CONDENSATION OF COMPOUND GASES.



THE following table may be found useful in several instances, wherefore we have extended it more than is required for analytical purposes. In the first column the reader will find the name of the gases; in the second, the elements of the compound gases indicated in volumes; in the third, their rate of condensation, or the ratio of volumes occupied by these gases taken together before or after their condensation under a same temperature and pressure; in the fourth and the fifth, the found and the calculated specific gravity of all the gases mentioned in the first column; in the nine other columns, their absolute weight expressed in grammes for 1000 to 9000 cubic centimetres at 0° cent. temperature, and 0·76 metre of barometric height. Vapours have been taken account of as gases, because they differ from the latter only by the greater ease with which they are condensed into the liquid or solid state. The specific weights of the vapours, especially those of an organic nature, which have been determined of late are so very numerous, that had we admitted them all they would have taken up too much room; we have, therefore, limited their enumeration to the most important among them.

The usefulness of this table will be better understood from the following explanations:—

1st COLUMN.—*Names of the Gases.*—All the substances, either simple or compound, which are admitted in this column must be supposed in the gaseous state. Among the simple substances,

Arsenic,	Mercury,
Bromine,	Oxygen,
Chlorine,	Sulphur,
Iodine,	Nitrogen, and
Phosphorus,	Hydrogen,

are the only ones which have been weighed directly in the state of gases.

With respect to—

Antimony,	Carbon,
Boron,	Selenium,
Chromium,	Titanium, and
Fluorine,	Tin,
Silicium,	

the determination of the specific gravity of their gases has been deduced, by more or less peremptory reasons, from the gaseous combinations which they form with other bodies. It is possible, therefore, that further researches may render many modifications necessary.

Among the compound substances, several of them are either quite hypothetical or have not been as yet isolated, or else have not been obtained or weighed in the gaseous state.

2nd COLUMN.—*Elements of one Volume of the Compound Gas.*

These elements are indicated in volumes, and therefore all the numbers placed before their symbols are indicative of volumes or of measures, and not of atomic weights as usual.

The composition of some combinations, such as mentioned in this column, will be found different from that which is admitted usually in atomic weights; the reason of this is as follows: Hitherto it has been admitted that the specific weight of the elementary gases, that is to say their absolute weight for a same volume, a same pressure, and a same temperature, bears a

proportion to the atomic weights; or, in other words, that equal volumes of the elements when brought to the gaseous state invariably contain the same number of these atoms of elements at a same temperature and pressure. In this hypothesis the quantities of the atoms contained in two measures of any kind of gas of a different size would be directly as the size of these measures. So long as only specific weight of the elements usually in the gaseous state were known, namely of oxygen, nitrogen, hydrogen, and chlorine, this very simple hypothesis was quite satisfactory, and chemists were justified in taking it as a rule for the determination of the atomic weight of hydrogen; and accordingly, as aqueous vapour consists of two volumes of oxygen and one volume of hydrogen, water was considered as being, likewise, composed of two atoms of hydrogen and of one atom of oxygen, although it was quite as rational, as done by English chemists, to consider it as composed of an equal number of atoms of the two elements, supposing the weight of the atom of hydrogen double that which is ordinarily admitted for this body.

Some new elementary non-permanent gases having been recently weighed by Dumas and Mitscherlich, however, have proved that this hypothesis is untenable; or, at least, that, in order to support the atomic weights of many substances, it must be very seriously modified in an almost unwarrantable manner. It has been ascertained, in effect, that gaseous sulphur is three times heavier, in gaseous phosphorus, and arsenic twice heavier, and gaseous mercury one half heavier, than was supposed in the hypothesis in question. In order, therefore, to maintain that the weight of an atom of sulphur is equal to the weight of a volume of the same body, we should be compelled to consider sulphuric acid as resulting from the combination of one atom of sulphur with nine atoms of oxygen. It therefore appears more in conformity with the present state of science to establish a distinction between the atomic weight of the elements and their specific gravity in the gaseous form, and consequently to admit that a similar volume of elementary gases, at a same temperature

and pressure, does not contain the same number of atoms as was always admitted to be the case for compound gases. Let us suppose, for example, that at  $0^{\circ}$  cent. and 0.76 of barometric height, one cubic centimetre of oxygen contains 100 atoms of oxygen, the inference is that, under the same circumstances, one cubic centimetre of sulphur contains 300 atoms of sulphur, one cubic centimetre of phosphorus or of arsenic 200 atoms of phosphorus or of arsenic, one cubic centimetre of mercury 50 atoms of mercury. In support of this atomic theory, it may be said that, judging from the data furnished by experiment, the specific weights of the elementary gases which have been observed, when they do not agree with those which are calculated directly from the atomic weights, are always, at least very approximatively so, multiples or submultiples thereof by whole numbers.

This last circumstance enables us to deduce the specific from their atomic weights, and this more accurately than is done by direct weighing, provided only that the operator has discovered, by experiment, the whole number by which the atomic weight must be multiplied or divided. The specific weight of the elementary gas may thus be immediately found compared with that of oxygen taken as 1; it is sufficient to multiply by the specific weight of oxygen gas, such as it is determined, compared with that of the atmospheric air taken as 1, that is to say, by 1.1026, to obtain that of the elementary gas compared likewise to that unit. Almost all the specific weights of the elementary gases in the table have been thus obtained, except those of oxygen, nitrogen, and hydrogen, for which we have given, in the fourth column, the results of the extremely accurate weighings performed by Berzelius and Dulong.

With respect to the elements of boron, chromium, fluorine, silicium, carbon, titanium, and tin, which could not as yet be obtained in the state of gas, and which consequently could not be weighed as such, we have, for want of better methods, admitted that the atomic weight of their gases are directly as the weights of their atoms. As to gaseous antimony,

a specific weight has been admitted double that which is deduced from the atomic weight of that body, because, from its analogy with gaseous arsenic, this hypothesis appears most probable. On the other hand, the specific weight of gaseous selenium has been reckoned only at half that of its atomic weight, because this furnishes the simplest data of the composition of the vapour of selenious acid ; but of course all this is, for the present, nothing more than mere hypothesis.

That column, however, shows how many volumes of the constituents of a compound gas are, in reality, or most probably, contained in one volume of that same compound gas, and if these constituents are themselves of a compound nature, how many volumes of elementary gases are present to form both these constituents, and the gas resulting from their combination. It is found, for example, that one volume of hydrocyanic acid is immediately composed of half a volume of carbon gas, and half a volume of water, and mediately of half a volume of nitrogen gas and half a volume of hydrogen gas. In the same manner it is seen that one volume of anhydrous sulphuric acid contains either one-sixth part of sulphur in volume, and nine-sixths of oxygen in volume, or else one volume of sulphurous acid, and half a volume of sulphur. Gaseous ether is another example of the case ; one volume of this gas is composed of two volumes of gaseous carbon, five volumes of hydrogen gas, and half a volume of oxygen, or of two volumes of etherine and one volume of aqueous gas, or one volume of ethyle and half a volume of oxygen gas.

We should remark, however, in reference to the gases of the substances called organic, such as ether, alcohol, &c., that the binary composition indicated in the column is quite hypothetical, although the two substances which exist as surmised in such a composition are well known, and have actually been weighed in the gaseous state. The manner in which elements are grouped, even in inorganic compounds, is quite conjectural, and, therefore, we should be much more cautious in respect to



organic compounds, which we are enabled, it is true, to reduce, by decomposing them, into the constituents indicated, but which we have as yet no means of recomposing by synthesis with the same constituents. The binary compositions ascribed to the organic gases, should, therefore, be looked upon merely as useful signs for ulterior comparisons. That the specific weights calculated from these compositions agree with those actually found by experiment, is no proof of their correctness, for a multitude of such compositions may be imagined, all possessing the same property; and even the immediate composition of these gases reduced to their elements, always gives the same result. Thus, for example, by doubling the specific weight of gaseous carbon, quintupling that of hydrogen gas, and taking half that of oxygen gas, the sum-total of these products gives the specific weight of gaseous ether, quite as well as by simply adding the weight of water to double that of the specific weight of etherine or of olefiant gas, or by adding half the specific weight of oxygen gas to that of the specific weight of ethyle.

With respect to atmospheric air, which must be considered as a simple mixture, no composition has been indicated. According to Brunner, it contains 0.209 volume of oxygen, and 0.791 volume of nitrogen. According to Saussure, 0.00415 volume of carbonic acid should be deducted from the latter as an average number in the open air. The air of apartments, which is always a little richer in carbonic acid than the open air, may, therefore, be considered in the dry state as being composed of 0.209 volume of oxygen gas, 0.786 volume of nitrogen gas, and 0.5 volume of carbonic acid per cent. To the specific weight of such mixture, that of the other gases have hitherto been compared, because it would appear that in these weighings the air could never be completely freed from its carbonic acid. This quantity of carbonic acid is too trifling, it is true, to affect much the specific weight of the air; for by admitting, as has been hitherto

- done = 1 a dry air, containing 0.005 in volume of this acid, the air free from carbonic acid = 0.99737. But the influence

becomes very considerable when we wish to calculate the quantity of the constituents of the air from their specific weights. Let us admit that the air contains no carbonic acid, we find by such a calculation 0.18957 volume of oxygen gas, and 0.81043 volume of nitrogen gas; but if we admit 0.005 of carbonic acid in the air, we find that the 0.995 volume remaining, consists of 0.2102 volume of oxygen, and 0.7848 volume of nitrogen, which ratio comes very near the data furnished by experiment.

We should explain also why, in that column, when the constituents of a volume of compound gases are fractional numbers, these fractions very often have not been reduced to their simplest expression, and have always been given with the same denominators. The only object in view was to facilitate the appreciation of the ratios. For example, speaking of chloride of phosphorus, it is there stated, that one volume of that body contains  $\frac{1}{3}$  volume of phosphorus and  $\frac{10}{6}$  volumes of chlorine, whereby it is immediately perceived, at one glance, that phosphorus and chlorine are in volumes=1:10, that one volume of gaseous phosphorus and ten volumes of gaseous chlorine, consequently eleven volumes of constituents give, after their combination, six volumes of chloride of phosphorus gas. Had we calculated the composition of that substance by  $\frac{1}{3}$  volume of gaseous phosphorus and  $\frac{10}{3}$  volumes of gaseous chlorine, it would have been, of course, quite as correct, but the ratio would have been less evident.

3d COLUMN.—This column contains a peculiar element of the compound gases, and which may establish an essential difference between two combinations of a perfectly similar composition with respect to the ratio in weight of their constituents, namely, the ratio of a volume occupied by the constituents of a gas, taken together, before and after their combination. This ratio has been called in the Table, simply, Ratio of Condensation, because in most cases, in effect, the constituents taken together, have a greater volume before their chemical union than after,

and, consequently, a condensation has taken place. There are, however, cases when the contrary happens, that is to say, there is dilatation, and the constituents taken together have a greater volume after than before their combination. Hitherto, only one case of the kind has been detected by experiment, which is that of gaseous cinnabar, in which a dilatation of 7 : 9 is observed. If the hypothetical specific weight admitted for carbon is correct, a similar dilatation should also take place with sulphuret of carbon. It is worthy of remark, that dilatations of an analogous nature occur in certain solid combinations in which changes of bulk, much less considerable it is true, are observed in the sum of their constituents before and after their union; such is the case, for example, according to Boullay, with subiodide and periodide of mercury, and iodide of lead. But here the phenomena are more complex, since they are referrible to the crystalline form of the constituents and of their combinations.

The ratios of condensation which I have indicated always refer, as I have said, to the constituents taken together, and not to these constituents separately. Except the two cases above alluded to, the sum of the constituents is always condensed; but the constituents themselves may have undergone condensation or dilatation, or have remained in the same state. In gaseous anhydrous sulphuric acid, the constituents taken together have undergone condensations in the proportion of 10 : 6; but the oxygen gas has condensed only in that of 9 : 6, and the sulphur, on the contrary, in that of 1 : 6. In sulphuretted hydrogen, the sulphur has undergone the same condensation, but the hydrogen gas has undergone no change. As to those gases, the binary elements of which are compound, as, for example, ether and alcohol, the ratio of condensation indicated refers not to the remote constituents, but to their proximate constituents, and to their sum total, as always. According to the binary combination admitted for such a gas, the condensation varies; if gaseous alcohol be considered

as a compound of etherine and of aqueous vapour, the ratio of condensation is 2 : 1 ; if considered as being a compound of ether and of water, this ratio is 1 : 1, that is to say, the combination has been attended with no condensation. If it is wished to take into consideration only the condensations or dilatations of the elements of gaseous alcohol, we have  $C_1H_3 O_{\frac{1}{2}}$ ; whence it follows that the gas of carbon has not condensed, that the hydrogen gas has condensed three times, and the oxygen gas has dilated twice.

We have remarked already that the degree of condensation of the constituents may establish a difference between two compound gases, the nature and proportion of the constituents of which are otherwise the same. Etherine or olefiant gas, and the quadricarburet of Faraday are examples of the case. Both consist of carbon gas and of hydrogen gas in the proportion of 1 : 2, but the quadricarburet contains a volume of these two gases, which is double that which exists in olefiant gas ; consequently the ratio of condensation, referring, as always, to the sum of the constituents, is double in the first gas what it is in the second. Therefore one volume of olefiant gas requires three volumes of oxygen for its complete combustion, whilst one volume of quadricarburetted hydrogen gas requires six volumes of oxygen.

By means of the columns 2 and 3 a great number of instructive cases may be observed. Thus, for example, we see that oxygen gas undergoes no change of volume when, by absorbing carbon, it becomes converted into carbonic acid, but that by absorbing double the quantity of carbon, it becomes oxyde of carbon, and then doubles its volume. We see also, that when we abstract sulphur from hydrosulphuric acid gas by heating it with a metal, the volume of hydrogen left remains the same ; but if, on the contrary, we pass hydrochloric acid gas over a metal, only half the volume of hydrogen remains ; on the other hand, if we remove the phosphorus from an equal

volume of phosphuretted hydrogen gas, we obtain one volume and a half of hydrogen gas as residue. We see also, that three volumes of oxygen are required to become completely one volume of olefiant gas, because this gas contains one volume of carbon gas, and two volumes of hydrogen gas, the first of which requires two volumes, and the second one volume of oxygen gas, to become converted into carbonic acid and water. For the same reason, the complete combustion of one volume of oxyde of carbon requires half a volume of oxygen gas. Lastly, we have likewise indicated in the third column for the gases of simple substances, how many atoms are respectively contained in one volume; we thus see, for example, that there are two atoms in the gas of antimony, and of arsenic, whilst that of mercury, and of selenium, contain only one-half atom.

4th COLUMN—(*Specific Weight—(found)*). The numbers of this column are the results of most accurate weighings. From the blanks left, the reader may know what are the gases the specific weights of which are as yet hypothetical.

5th COLUMN—(*Specific Weight—(calculated)*). All the specific weights mentioned in this column, except those of oxygen, hydrogen, and nitrogen gases, have been deducted, as was said before, from the atomic weights, and are compared with the specific weight of atmospheric air. Should it be desired to compare or refer it to the specific weight of oxygen, all the numbers would have to be divided by that weight.

6TH TO 14TH COLUMN.—(*Absolute Weight of the Gases*).—The advantages of the decimal system being acknowledged, and the fundamental weighings having been made according to that system, we have employed it also here. The first of these columns contains the weight expressed in grammes, of a litre or 1000 cubic centimetres of each gas, at a pressure of 0.76 metre (mean pressure of places slightly above the level of the sea), and at the temperature of 0° cent. At that temperature the

vapours, of which the majority of the gases enumerated in the Table consist, cannot, it is true, support the pressure of 0·76 without being brought to the liquid or to the solid state, so that the weights assigned to them in that column are ideal quantities. Yet, with the help of the law of Mariotte, and of the law discovered by Gay Lussac and Rudberg for the dilatation of the gases by heat, it is easy to find from that number the weights of the gases in question, for the temperature at which they really equilibrate the atmospheric pressure, or, in general, any pressure whatever. Suppose, for example, that we should wish to know the weight of 1000 cubic centimetres of an aqueous vapour which, at 100° cent. supports a column of mercury 0·76 metre high, it suffices to divide the weight of 0·80556 gramme, indicated in the column, by 1·365 (increase of each volume of the gas, from 0° to 100° cent.) In general, when the temperature is not 0°, but is another temperature, no matter which,  $t$ , and the pressure is not 0·76 metre, but is another pressure, no matter which,  $p$ , the weight 1000 cubic centimetres of a gas is found by dividing that which it has at 0° cent. and 0·76 metre by  $1 + 0·0365 t$ , and multiplying by  $\frac{p}{0·76}$ . But, however, the weight 1000 cubic centimetres of gas at 0° cent. and 0·76 metre, contained in the column, are multiplications of the specific weights contained in the fifth column, by the weight of an equal volume of dry atmospheric air, under the same conditions, which weight, according to the weighings of Biot, is 1·299075 gramme.

The use of the latter columns will be rendered more clear by an example. Let us suppose that, with Liebig and Wöhler, we have burnt cyanic ether with protoxyde of copper, and that, after reducing at 0° cent. and 0·76 metre, we have thus obtained 120 cubic centimetres of a gas which, being decomposed by hydrate of potash, is found to be composed of four volumes of carbonic acid and one volume of nitrogen gas. Query.—How much cyanogen and how much carbon are contained in cyanic ether? We see by the second column that one volume of

carbonic acid contains half a volume of carbon, and that one volume of cyanogen contains one volume of nitrogen and one volume of carbon. The 24 cubic centimetres of nitrogen gas found, correspond therefore to 24 cubic centimetres of cyanogen; and these, according to the seventh and ninth columns, weigh 6.0566706 grammes. There are, besides, in 24 cubic centimetres of cyanogen, 24 cubic centimetres of carbon, which correspond to 48 cubic centimetres of carbonic acid; these being deducted from 96 cubic centimetres, of carbonic acid found, there remains 48 cubic centimetres, and, consequently, 24 cubic centimetres for the carbon which was not combined with the nitrogen. The weight of these 24 cubic centimetres of carbon taken from the seventh and ninth columns, is 0.0262764 gramme.

It is known that cyanic ether may be considered as composed ether of cyanuric acid and alcohol, or of cyanuric acid, of ether, and of water. It may therefore be asked how much alcohol or ether are indicated by these 24 cubic centimetres of carbon. By the 2nd column, it is seen that one volume of vapour of alcohol contains one volume of carbon gas, and that one volume of vapour of ether contains two volumes of carbon gas. Therefore, 24 cubic centimetres of carbon gas correspond to 24 cubic centimetres of vapour of alcohol, and the weight of the latter, taken from columns VII. and XI. is 0.04990008 gramme. Moreover, 24 cubic centimetres of carbon gas correspond to 12 cubic centimetres of vapour of ether, which weigh also, according to the same columns, 0.04023336 gramme.

This method of deducing the quantities in weight from the volumes, presupposes that the gases are dry, for the column gives, of course, only the weight of the gases in the dry state. If, however, the gas is moist, its weight may also be ascertained by means of this Table; it is only necessary, by adding an excess of water, to bring it to the maximum of moisture, and to observe carefully at the same time the temperature and pressure to which it is exposed. The operator, next, has to find what portion of this pressure is equilibrated by the tension of the aqueous vapour at the temperature observed, and

deducting this fraction of pressure from the total pressure, the pressure experienced by the dry gas is attained, and hence the weight of the latter is easily found. Let us suppose that we have 90 cubic centimetres of perfectly moist carbonic acid, at  $20^{\circ}$  cent., and 757.31 millimetres pressure; we find that 17.3 millimetres thereof belong to the tension of the aqueous vapour. The dry carbonic acid is, therefore, under a pressure of 740 millimetres. The weight of 90 cubic centimetres of carbonic acid, as indicated in the following Table, that is 0.17818, must, therefore, be multiplied by 740, and divided by 760. But as the acid has likewise a temperature of  $20^{\circ}$  cent., we must, moreover, divide the weight thus obtained by  $(1 + 0.0365 \ 20)$ . It is thus found that the weight of 90 cubic centimetres of carbonic acid, at  $20^{\circ}$  cent., 740 millimetres of the barometer = 0.16139 gramme. But it is always better to desiccate the gases, because water always absorbs a little gas, and when they are very soluble, the tension of the vapour of the solution is no longer equal to that of the tension of pure aqueous vapour.



Names of Gases.	Constituent or Component parts of a Volume of the Gases.	Product of Condensation.	Specific Weight.		Absolute Weight, in Grammes, to 0° C. and 0.76 Metre, of Cubic Centimetres.								
			Found	Calculated.	1000	2000	3000	4000	5000	6000	7000	8000	9000
Alcohol . . .	$\text{CH}_3\text{O} \frac{1}{2}$	9 : 2	1.6133	1,60049	2,07916	4,15832	6,23748	8,31664	10,39580	12,47496	14,55412	16,63328	18,71244
Hydrate of Eth. . .	$\text{C}_2\text{H}_5\text{O} \frac{1}{2} + \text{HO} \frac{1}{2}$	1 : 1	0.5967	0,59120	0,76801	1,53602	2,30403	3,07204	3,84005	4,60806	5,37607	6,14408	6,91209
Ammonia . . .	$\frac{1}{2}\text{N} + \frac{3}{2}\text{H}$	2 : 1	0.5967	17,78388	23,10260	46,20520	69,30780	92,41040	115,51300	138,61560	161,71820	184,82080	207,92340
Antimony . . .	$\frac{1}{4}\text{Sb} + \frac{3}{4}\text{H}$	7 : 4	10.65	4,54917	5,90972	11,81944	17,72916	23,63888	29,54860	35,45832	41,36804	47,27776	53,18748
Antimonietted Hy . .	$\frac{1}{4}\text{As} + \frac{3}{4}\text{H}$	7 : 4	10.65	10,36536	13,46538	26,93076	40,39614	53,86152	67,32690	80,79228	94,25766	107,72304	121,18842
Arsenic . . .	$\frac{1}{4}\text{As} + \frac{3}{4}\text{H}$	7 : 4	2.695	2,69454	3,50041	7,00082	10,50123	14,00164	17,50205	21,00246	24,50287	28,00328	31,50369
Arseniuretted Hy . .	$\frac{1}{4}\text{As} + \frac{3}{4}\text{H}$	7 : 4	13.85	13,67316	17,76247	35,52494	53,28741	71,04988	88,81235	106,57482	124,33729	142,09976	159,86223
Arsenious Acid . .	$\text{As} + 3\text{O}$	3 : 1	1.000	1,00000	1,299075	2,598150	3,897225	5,196300	6,495375	7,794450	9,093525	10,392600	11,691675
Atmospheric Air . .			1.000	1,00000	1,299075	2,598150	3,897225	5,196300	6,495375	7,794450	9,093525	10,392600	11,691675
Boron . . .	B	1	1.9934	1,99776	3,99552	5,94328	7,79104	9,73880	11,68656	13,63432	15,58208	17,52984	19,47760
Bromine . . .	Br	1	5.54	5,39337	7,00639	14,01278	21,01917	28,02556	35,03195	42,03834	49,04473	56,05112	63,05751
Carbon . . .	C	1	1.524	0,84279	1,09485	2,18970	3,28455	4,37940	5,47425	6,56910	7,66395	8,75880	9,85365
Carbonic Acid . .	$\frac{1}{2}\text{C} + \text{O}$	3 : 2	1.524	1,62400	1,97978	3,95956	5,93934	7,91912	9,89890	11,87868	13,85846	15,83824	17,81802
Carbonic Oxide . .	$\frac{1}{2}\text{C} + \frac{1}{2}\text{O}$	1 : 1	0.9409	0,97269	1,26360	2,52720	3,79080	5,05440	6,31800	7,58160	8,84520	10,10880	11,37240
Carburet of Sulph. .	$\frac{2}{3}\text{S} + \frac{1}{3}\text{C}$	5 : 6	2.6447	2,63944	3,42883	6,85766	10,28649	13,71532	17,14415	20,57298	24,00181	27,43064	30,85947
Chloride of Antim. .	$\frac{1}{2}\text{Sb} + \frac{3}{2}\text{Cl}$	7 : 4	7.3	8,10647	10,53090	21,06180	31,59270	42,12360	52,65450	63,18540	73,71630	84,24720	94,77810
Chloride of Arsen. .	$\frac{1}{2}\text{As} + \frac{3}{2}\text{Cl}$	7 : 4	6.3066	6,25163	8,12161	16,24322	24,36483	32,48644	40,60805	48,72966	56,85127	64,97288	73,09449
Chloride of Boron . .	$\frac{1}{2}\text{B} + \frac{3}{2}\text{Cl}$	7 : 4	3.942	4,03532	5,24220	10,48440	15,72660	20,96880	26,21100	31,45320	36,69540	41,93760	47,17980
Chloride of Phos. .	$\frac{1}{2}\text{P} + \frac{3}{2}\text{Cl}$	11 : 6	4.85	4,78814	6,25016	12,44032	18,66048	24,88064	31,10080	37,32096	43,54112	49,76128	55,98144
Chloride of Silic. .	$\frac{1}{2}\text{Si} + \frac{3}{2}\text{Cl}$	7 : 3	5.939	5,90049	7,65517	15,33034	22,99551	30,66068	38,32585	45,99102	53,65619	61,32136	68,98653
Chloride of Sulph. .	$\frac{1}{2}\text{S} + \text{Cl}$	4 : 3	4.70	4,65838	6,05158	12,10316	18,15474	24,20632	30,25790	36,30948	42,36106	48,41264	54,46422
Chloride of Tin . .	$\frac{1}{2}\text{Sn} + 2\text{Cl}$	5 : 2	9.1997	8,93433	11,60639	23,21278	34,81917	46,42556	58,03195	69,63834	81,24473	92,85112	104,45751
Chloride of Titan. .	$\frac{1}{2}\text{Ti} + 2\text{Cl}$	5 : 2	6.836	6,55488	8,51528	17,03056	25,54584	34,06112	42,57640	51,09168	59,60696	68,12224	76,63752
Chlorine . . .	Cl.	1	2.47	2,44033	3,17017	6,34034	9,51051	12,68068	15,85085	19,02102	22,19119	25,36136	28,53153
Chromium . . .	Cr	1	7.1	3,87916	5,03932	10,07864	15,11796	20,15728	25,19660	30,23592	35,27524	40,31456	45,35388
Cyanogen . . .	C + N	2 : 1	1.8064	1,81879	2,36275	4,72550	7,08825	9,45100	11,81375	14,17650	16,53925	18,90200	21,26475
Ether . . .	$\text{C}_2\text{H}_5\text{O} \frac{1}{2}$	15 : 2	2.586	2,58088	3,35276	6,70552	10,05828	13,41104	16,76380	20,11656	23,46932	26,82208	30,17484
Hydrate of Eth. . .	$2\text{CH}_3 + \text{HO} \frac{1}{2}$	3 : 1	0.9852	0,98039	1,27360	2,54720	3,82080	5,09440	6,36800	7,64160	8,91520	10,18880	11,46240
Oxide of Ethyle . .	$\text{C}_2\text{H}_5 + \text{O} \frac{1}{2}$	3 : 2	0.9852	1,28894	1,67443	3,34886	5,02329	6,69772	8,37215	10,04658	11,72101	13,39544	15,06987
Ether-olefant gas. .	$\text{CH}_2$	3 : 1	0.556	0,55900	0,72619	1,45238	2,17857	2,90476	3,63095	4,35714	5,08333	5,80952	6,53571
Fluorine . . .	$\frac{1}{2}\text{C} + 2\text{H}$	5 : 2	4.44	4,38495	5,69639	11,39278	17,08917	22,78556	28,48195	34,17834	39,87473	45,57112	51,26751
Gas of marshes . .	$\frac{1}{2}\text{I} + \frac{1}{2}\text{H}$	1 : 1	4.44	4,38495	5,69639	11,39278	17,08917	22,78556	28,48195	34,17834	39,87473	45,57112	51,26751
Hydriodic Acid . .	$\frac{1}{2}\text{I} + \frac{1}{2}\text{H}$	1 : 1	4.44	2,73107	3,54788	7,09576	10,64864	14,19152	17,73840	21,28728	24,83616	28,38304	31,93092
Hydrobromic Ac. .	$\frac{1}{2}\text{Br} + \frac{1}{2}\text{H}$	1 : 1	4.44	2,73107	3,54788	7,09576	10,64864	14,19152	17,73840	21,28728	24,83616	28,38304	31,93092

Hydrochloric Ac.	1:1	1,2474	1,25456	1,62977	3,25954	4,88931	6,51908	8,14885	9,77862	11,40839	13,03816	14,66793
Hydrocyanic Ac.	1:1	0,9476	0,94379	1,22606	2,45212	3,67818	4,90424	6,13030	7,35636	8,58242	9,80848	11,03454
Hydrofluoboric Acid.	7:4	2,3124	2,30824	2,99858	5,99716	8,99574	11,99432	14,99290	17,99148	20,99006	23,98864	26,98722
Hydrofluoric Ac.	1:1	0,67887	0,67887	0,88190	1,76380	2,64570	3,52760	4,40950	5,29140	6,17330	7,05520	7,93710
Hydrofluosilicic Ac.	7:3	3,600	3,59771	4,67369	9,34738	14,02107	18,69476	23,36845	28,04214	32,71583	37,38952	42,06321
Hydrogen.	1	0,0688	0,06880	0,06938	0,17876	0,26814	0,35752	0,44690	0,53628	0,62566	0,71504	0,80442
Iodine.	1	8,716	8,70111	10,30340	22,60680	33,91030	45,21360	56,51700	67,82040	79,12380	90,42720	101,73060
Ioduret of Arsenic	7:4	16,1	15,64300	20,32144	40,64288	60,96432	81,28576	101,60720	121,92864	142,25008	162,57152	182,89296
Ioduret of Merc.	2:1	16,2	15,67959	20,36697	40,73794	61,10691	81,47588	101,84485	122,21382	142,58279	162,95176	183,32073
Mercury	1	7,03	6,97848	9,06557	18,13114	27,19671	36,26228	45,32785	54,39342	63,45899	72,52456	81,59013
Nitric Oxide	1:1	1,03880	1,03930	1,35013	2,70026	4,05039	5,40052	6,75065	8,10078	9,45091	10,80104	12,15117
Nitrogen.	1	0,976	1,26790	2,53580	3,80370	5,07160	6,33950	7,60740	8,87530	10,14320	11,41110	12,67900
Nitrous Oxide	3:2	1,5204	1,52730	1,98408	3,96816	5,95234	7,93632	9,92040	11,90448	13,88856	15,87264	17,85672
Oxychlor. Chrom.	5:2	5,9	5,48251	7,12219	14,24438	21,36657	28,48876	35,61095	42,73314	49,85533	56,97752	64,09971
Oxygen.	1	1,1026	1,43236	2,86472	4,29708	5,72944	7,16180	8,59416	10,02652	11,45888	12,89124	14,32360
Perochlor. of Phos.	7:4	4,875	4,74109	6,16007	12,32014	18,48021	24,64028	30,80035	36,96042	43,12049	49,28056	55,44063
Phosgen Gas	2:1	4,875	3,41302	4,43377	8,86754	13,34131	17,73508	22,12885	26,52262	31,03639	35,47016	39,90393
Phosphorus.	2	4,58	4,32562	5,61930	11,23860	16,83730	22,47720	28,09650	33,71580	39,33510	44,95440	50,57370
Phosphuretted Hydrog. (the two kinds)	7:4	1,151	1,10460	1,58889	3,07778	4,61667	6,15556	7,69445	9,23334	10,77223	12,31112	13,85001
Protochlor. of Merc.	2:1	12,16	12,37185	16,07196	32,14392	48,21588	64,28784	80,35980	96,43176	112,50372	128,57568	144,64764
Proto-chlor. Merc	2:1	9,8	9,41881	12,23374	24,47148	36,70722	48,94296	61,17870	73,41444	85,65018	97,88592	110,12166
Quadrhydrocarb.	6:1	1,8	1,96078	2,54722	5,09444	7,64166	10,18888	12,73610	15,28332	17,83054	20,37776	22,92498
Selenious Acid.	2:1	4,03	3,82923	4,97446	9,94892	14,92338	19,89784	24,87230	29,84676	34,82122	39,79568	44,77014
Selenium.	1	4,03	2,72663	3,54210	7,08420	10,62650	14,16880	17,71050	21,25260	24,79470	28,33680	31,87890
Silicium.	1	3,05949	3,05949	1,32483	2,64966	3,97449	5,29932	6,62415	7,94898	9,27381	10,59864	11,92347
Sub-brom. of Merc.	3:2	10,11	9,67516	12,56876	25,13752	37,70688	50,27604	62,84380	75,41256	87,98132	100,55008	113,11884
Sub-chlor. of Merc.	3:2	8,35	8,19864	10,65065	21,30130	31,95195	42,60260	53,25325	63,90390	74,55455	85,20520	95,85585
Sulphur.	3	6,90	6,65415	8,64423	17,28846	25,93269	34,57692	43,22115	51,86538	60,50961	69,15384	77,79807
Sulphurett. Hydr.	7:6	1,1192	1,17782	1,53008	3,06016	4,59034	6,12032	7,65040	9,18048	10,71056	12,24064	13,77072
Sulphuret of Merc.	7:9	5,95	5,39167	7,00418	14,00836	21,01254	28,01672	35,02090	42,02508	49,02926	56,03344	63,03762
Sulphurous Acid.	7:6	2,247	2,21162	2,87306	5,74612	8,61918	11,49224	14,36530	17,23836	20,11142	22,98448	25,85754
Sulphuric Acid.	10:6	3,01	2,76292	3,58924	7,17848	10,76772	14,35696	17,94620	21,53544	25,12468	28,71392	32,30316
Tin	3:2	8,10735	10,59210	21,06420	31,59630	42,12840	52,66050	63,19260	73,72470	84,25680	94,77890	105,30104
Titanium	1	3,34844	3,34844	9,94892	14,92338	19,89784	24,87230	29,84676	34,82122	39,79568	44,77014	49,74468
Water	3:2	0,6235	0,62010	0,80556	1,61113	2,41668	3,22224	4,02780	4,83336	5,63892	6,44448	7,25004

TABLE FOR THE CONVERSION OF DEGREES ON THE CENTIGRADE  
THERMOMETER INTO DEGREES OF FAHRENHEIT'S SCALE.

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
300°	572.0	243°	469.4	186°	366.8	129°	264.2	72°	161.6	15°	59.0
299	570.2	242	467.6	185	365.0	128	262.4	71	159.8	14	57.2
298	568.4	241	465.8	184	363.2	127	260.6	70	158.0	13	55.4
297	566.6	240	464.0	183	361.4	126	258.8	69	156.2	12	53.6
296	564.8	239	462.2	182	359.6	125	257.0	68	154.4	11	51.8
295	563.0	238	460.4	181	357.8	124	255.2	67	152.6	10	50.0
294	561.2	237	458.6	180	356.0	123	253.4	66	150.8	9	48.2
293	559.4	236	456.8	179	354.2	122	251.6	65	149.0	8	46.4
292	557.6	235	455.0	178	352.4	121	249.8	64	147.2	7	44.6
291	555.8	234	453.2	177	350.6	120	248.0	63	145.4	6	42.8
290	554.0	233	451.4	176	348.8	119	246.2	62	143.6	5	41.0
289	552.2	232	449.6	175	347.0	118	244.4	61	141.8	4	39.2
288	550.4	231	447.8	174	345.2	117	242.6	60	140.0	3	37.4
287	548.6	230	446.0	173	343.4	116	240.8	59	138.2	2	35.6
286	546.8	229	444.2	172	341.6	115	239.0	58	136.4	+ 1	33.8
285	545.0	228	442.4	171	339.8	114	237.2	57	134.6	0	32.0
284	543.2	227	440.6	170	338.0	113	235.4	56	132.8	- 1	30.2
283	541.4	226	438.8	169	336.2	112	233.6	55	131.0	- 2	28.4
282	539.6	225	437.0	168	334.4	111	231.8	54	129.2	- 3	26.6
281	537.8	224	435.2	167	332.6	110	230.0	53	127.4	- 4	24.8
280	536.0	223	433.4	166	330.8	109	228.2	52	125.6	- 5	23.0
279	534.2	222	431.6	165	329.0	108	226.4	51	123.8	- 6	21.2
278	532.4	221	429.8	164	327.2	107	224.6	50	122.0	- 7	19.4
277	530.6	220	428.0	163	325.4	106	222.8	49	120.2	- 8	17.6
276	528.8	219	426.2	162	323.6	105	221.0	48	118.4	- 9	15.8
275	527.0	218	424.4	161	321.8	104	219.2	47	116.6	- 10	14.0
274	525.2	217	422.6	160	320.0	103	217.4	46	114.8	- 11	12.2
273	523.4	216	420.8	159	318.2	102	215.6	45	113.0	- 12	10.4
272	521.6	215	419.0	158	316.4	101	213.8	44	111.2	- 13	8.6
271	519.8	214	417.2	157	314.6	100	212.0	43	109.4	- 14	6.8
270	518.0	213	415.4	156	312.8	99	210.2	42	107.6	- 15	5.0
269	516.2	212	413.6	155	311.0	98	208.4	41	105.8	- 16	3.2
268	514.4	211	411.8	154	309.2	97	206.6	40	104.0	- 17	+ 1.4
267	512.6	210	410.0	153	307.4	96	204.8	39	102.2	- 18	- 0.4
266	510.8	209	408.2	152	305.6	95	203.0	38	100.4	- 19	- 2.2
265	509.0	208	406.4	151	303.8	94	201.2	37	98.6	- 20	- 4.0
264	507.2	207	404.6	150	302.0	93	199.4	36	96.8	- 21	- 5.8
263	505.4	206	402.8	149	300.2	92	197.6	35	95.0	- 22	- 7.6
262	503.6	205	401.0	148	298.4	91	195.8	34	93.2	- 23	- 9.4
261	501.8	204	399.2	147	296.6	90	194.0	33	91.4	- 24	- 11.2
260	500.0	203	397.4	146	294.8	89	192.2	32	89.6	- 25	- 13.0
259	498.2	202	395.6	145	293.0	88	190.4	31	87.8	- 26	- 14.8
258	496.4	201	393.8	144	291.2	87	188.6	30	86.0	- 27	- 16.6
257	494.6	200	392.0	143	289.4	86	186.8	29	84.2	- 28	- 18.4
256	492.8	199	390.2	142	287.6	85	185.0	28	82.4	- 29	- 20.2
255	491.0	198	388.4	141	285.8	84	183.2	27	80.6	- 30	- 22.0
254	489.2	197	386.6	140	284.0	83	181.4	26	78.8	- 31	- 23.8
253	487.4	196	384.8	139	282.2	82	179.6	25	77.0	- 32	- 25.6
252	485.6	195	383.0	138	280.4	81	177.8	24	75.2	- 33	- 27.4
251	483.8	194	381.2	137	279.6	80	176.0	23	73.4	- 34	- 29.2
250	482.0	193	379.4	136	277.8	79	174.2	22	71.6	- 35	- 30.0
249	480.2	192	377.6	135	275.0	78	172.4	21	69.8	- 36	- 32.8
248	478.4	191	375.8	134	273.2	77	170.6	20	68.0	- 37	- 34.6
247	476.6	190	374.0	133	271.4	76	168.8	19	66.2	- 38	- 36.4
246	474.8	189	372.2	132	269.6	75	167.0	18	64.4	- 39	- 38.2
245	473.0	188	370.4	131	267.8	74	165.2	17	62.6	- 40	- 40.0
244	471.2	187	368.6	130	266.0	73	163.4	16	60.8		

## FRENCH WEIGHTS AND MEASURES.

## MEASURES OF WEIGHT.

FRENCH.	ENGLISH GRAINS.
Milligramme = . . . . .	.0154
Centigramme = . . . . .	.1543
Decigramme = . . . . .	1.5434
Gramme = . . . . .	15.4336
Decagramme = . . . . .	154.3360
Hectogramme = . . . . .	1543.3600
Kilogramme = . . . . .	15433.6000
=	2.679 lbs. Troy.
=	2.205 lbs. Avoirdupois.

## MEASURES OF LENGTH.

	ENGLISH INCHES.
Millimètre = . . . . .	.03937
Centimètre = . . . . .	.39371
Decimètre = . . . . .	3.93710
Mètre = . . . . .	39.37100
Decamètre = . . . . .	393.71000
Hectomètre = . . . . .	3937.10000
Kilomètre = . . . . .	39371.00000
Myriomètre = . . . . .	393710.00000

## MEASURES OF CAPACITY.

	CUBIC INCHES.
Millitre = . . . . .	0.06112
Centilitre = . . . . .	0.61120
Decilitre = . . . . .	6.11208
Litre = . . . . .	61.12079
Decalitre = . . . . .	611.20792
Hectolitre = . . . . .	6112.07920
Kilolitre = . . . . .	61120.79208
Myriolitre = . . . . .	61120.792080

**THE END.**

LONDON :  
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**A**  
**PRACTICAL TREATISE**  
**OF**  
**CHEMICAL ANALYSIS.**



▲

PRACTICAL TREATISE

OF

CHEMICAL ANALYSIS,

INCLUDING

TABLES FOR CALCULATIONS IN ANALYSIS.

BY H. ROSE.

◆

TRANSLATED FROM THE FRENCH AND FROM THE FOURTH GERMAN EDITION.

*With Notes and Additions.*

BY A. NORMANDY.

IN TWO VOLUMES.

VOL I.

QUALITATIVE

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## ERRATA TO VOL. I.

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Preface, page vii, line 5 from the bottom, *for* "forensic," *read* "foreign."

Note 1st, page 48, *for* "as with potash," *read* "as with alumina."

Note 1st, page 136, line 2, *delete* "or ammonia;" and *for* "is a subsalt of mercury combined with the ammoniacal compound," *read* "is a double compound of protochloride of mercury (sublimite) with amidide of mercury.  
$$2 \text{ Hg Cl} + \text{Hg NH}_2 = (\text{Hg Cl} + \text{Hg NH}_2) + \text{H Cl}."$$

Page 255, line 8, *for* "bromide," *read* "bromate."

Page 179, line 14, *for* "Bisulphate," *read* "Bisulphuret."

Page 515, line 10, *for* "protochloride," *read* "protoxyde."



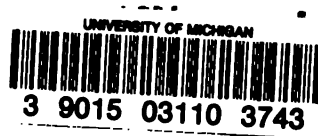








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